



Digitized by the Internet Archive
in 2010 with funding from
University of Toronto

The Journal of Industrial and Engineering Chemistry

PUBLISHED BY

The American Chemical Society

VOLUME V, 1913

Board of Editors

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

EASTON, PA.

ESCHENBACH PRINTING COMPANY

1913

142467
3 / 5 / 17

TP
1
I 13
v. 5

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

JANUARY, 1913

No. 1

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, Wm. McMurtrie, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Contributions and communications should be addressed to the Editor, M. C. Whitaker, Columbia University, New York City

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly.
Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

Morris Loeb's Will.....	2
The Code of Ethics of the American Institute of Chemical Engineers.....	2
Electrical Engineers' Resolutions Regarding Patent Legislation.....	4
Mineral Waste.....	5

ORIGINAL PAPERS:

The Production of Chlorine Substitution Products of Methane from Natural Gas. By Charles Baskerville and H. S. Riederer.....	5
Applications of Ductile Tungsten. By C. G. Fink.....	8
Blue Gelatine Copper. By Wilder D. Bancroft and T. R. Briggs.....	9
The Classification of Bituminous and Resinous Substances. By Herbert Abraham.....	11
The Effect of Exposure on Bitumens. By Prévost Hubbard and C. S. Reeve.....	15
Examples of the Efficiency of Calcium Hypochlorite in Treating Turbid Waters. By Edward Bartow.....	18
Composition of the Salines of the United States, III: Brines from the Ocean and Salt Lakes. By J. W. Turrentine, with analyses by W. H. Ross, A. R. Merz and R. F. Gardner.....	19
Recent Analyses of the Saratoga Mineral Waters. II. By Leslie Russell Milford.....	24
The Quantitative Separation of Mixtures of Certain Acid Coal Tar Dyes. By W. E. Mathewson.....	26
The Alcohol Requirement of the Pure Food and Drug Law and the Accuracy of Alcohol Assays of Pharmaceutical Preparations. By C. H. Briggs.....	29
The Mineralogical Analysis of Soils. By William H. Fry.....	30
The Significance of the Lime-Magnesia Ratio in Soil Analyses. By P. L. Gile and C. N. Ageton.....	33
A Proposed Modification of the Official Method of Determining Humus. By O. C. Smith.....	35
The Determination of Lime in Cow Feces. By R. Adams Dutcher.....	37

LABORATORY AND PLANT:

The Plant of the Sakai Celluloid Company at Sakai, Japan. By F. C. Axtell.....	38
Recent Developments in the Electric Steel Furnace. By P. L. V. Héroult.....	47
An Electric Heater for Laboratory Distillations. By L. T. Bryson.....	49

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS.....

ADDRESSES:

Protection of Intellectual Property in Relation to Chemical Industry. By L. H. Baekeland.....	51
The Permanent Fireproofing of Cotton Goods. By William Henry Perkin.....	57

Coal Tar Light Oil in the United States: The Manufacture, Nature and Uses of Products Derived Therefrom. By John Morris Weiss.....	61
The Past, Present, and Future of the Naval Stores Industry. By Charles H. Herty.....	65
The Technical Problems of Coal Preparation. By W. S. Ayres.....	68
The Beehive Coke Oven Industry of the United States. By A. W. Belden.....	71
American Oil Shales. By Chas. Baskerville.....	73

CURRENT INDUSTRIAL NEWS:

The Industrial Future of Maine.....	74
Reinforced Platinum.....	74
Iridium in American Placer Platinum.....	74
The Purchase of Lime for Water Purification.....	75
The Effect of Boiler Scale.....	75
Nitric Acid from Coke-oven Gases.....	75
The Electrotechnical Production of Ammonia.....	75
The Production of Calcium Carbide.....	75
The Japanese Window Glass Industry.....	75
Precautions in Handling Compressed Gases.....	76
Theta Tubing.....	76
The Production of Caoutchouc.....	76
A Water Temperature Regulator.....	76
Soap Lye and Saponification Crude Glycerins.....	77
The Production and Employment of Dextrin.....	77
Some Aspects of the French Turpentine Industry.....	77
The Disposition of Waste Sulphite Liquors.....	78
New Pressure Filters.....	79
The Purification of Water by "Allophanoids".....	79
"Electrit".....	79
The Utilization of Waste Soda Liquors.....	79
The Casein Industry.....	79

NOTES AND CORRESPONDENCE:

Obituary—William Willard Daniels.....	80
The Present Status of the Window Glass Industry.....	80
Centenary of the Gas Industry—Committee Report.....	81
Platinum Thief.....	82
Arkosite.....	83
Metallic Pigments.....	83
Surface Combustion.....	84
Annual Tables of Constants: Physical, Chemical and Technological, Volume II.....	84
The Determination of Chromium and Vanadium in Steel—A Correction.....	84
A New Form of Orsat Apparatus—A Note.....	84

BOOK REVIEWS:

Transactions of the American Institute of Chemical Engineers; The World's Cane Sugar Industry, Past and Present; Hydro-Metallurgy of Copper; Soil Conditions and Plant Growth; Henley's Twentieth Century Book of Recipes, Formulas and Processes.....	84
NEW PUBLICATIONS.....	87
RECENT INVENTIONS.....	88
MARKET REPORT.....	90

EDITORIALS

MORRIS LOEB'S WILL

Morris Loeb, whose death was reported in the November, 1912, issue of *THIS JOURNAL*, was known to be a man of great wealth only by his intimate friends. Few realized the diversity of his interests, and his philanthropic work was not known to many of his colleagues till after his death. His unassuming manner and genuine modesty were his best known characteristics.

The chemical profession was always a matter of deep concern to Morris Loeb. During his lifetime he was an active worker in the support of the chemical societies, the Chemists' Club, the education of chemists, and in fact all of the interests of chemistry, in addition to a multitude of philanthropic and social interests.

His will, which has just been made public, accentuates his true interest in the sciences. He has provided with directness, with simplicity, with modesty, but with magnificence. The bulk of his estate is to be transferred to his distinguished wife, Eda Kuhn Loeb. Harvard University, his Alma Mater, will receive, subject to the life interest of Mrs. Loeb, five hundred thousand dollars for the advancement of chemistry and physics in other ways than by payment of fellowships, scholarships and other direct emoluments to students.

The American Chemical Society is to receive twenty-five thousand dollars to be held by it as a special fund, the income of which alone shall be used for the establishment or maintenance of a chemical type-museum either in connection with the Chemists' Club of New York or the National Museum in Washington, or the American Museum of Natural History in New York—preference to be given in the order named. The chief object of this museum shall be the preservation of all new substances described as the result of chemical research, either by obtaining the same by gift or purchase from the discoverer, or by causing the same to be prepared in sufficient quantity according to the discoverer's published directions: all for the purpose of facilitating comparison by subsequent observers.

The Chemists' Building Company of New York is to receive Dr. Loeb's Chemists' Building Company stock which is valued at seventy-five thousand dollars. His magnificent private technical library, valued at fifty thousand dollars, his portraits and memorabilia of scientists, and scientific apparatus have all been given to the Chemists' Club.

The Hebrew Technical Institute, of New York City, receives twenty-five thousand dollars absolutely and twenty-five thousand dollars as a special fund, the income of which is to pay pensions of superannuated employees and of the families of employees who died in active service. The Jewish Publication Society of America gets ten thousand dollars. One thousand dollars each goes to the Young Women's Hebrew

Association, the Young Men's Hebrew Association, the Hebrew Educational Society of Brooklyn, the Hampton Industrial Institute, and the United Jewish Charities, and two thousand five hundred dollars to the National Academy of Sciences.

In addition to these specific bequests, Professor Loeb provided that to each charitable institution to which he contributed, a sum equal to the amount of his last contribution to such societies should be given for a period of two years after his death. To his servants he gave \$100 for each year that they had been in his service.

The residuary estate, subject to Mrs. Loeb's life interest, is to be equally divided among the Smithsonian Institution at Washington and the following New York institutions: The American Museum of Natural History, the Metropolitan Museum of Art, Cooper Union, the Hebrew Technical Institute, the New York Foundation, the Jewish Protectory and Aid Society, the Hebrew Charities Building, and the Educational Alliance.

The Smithsonian Institution receives its bequest to further the exact sciences. The American Museum of Natural History is to collect an exhibit for the illustration of the industrial use of natural products in ancient and modern times. The Metropolitan Museum of Art is to purchase and exhibit objects illustrating the development of artistic handicraft in Europe and America. Cooper Union is to endow a professorship. The Hebrew Technical Institute is to establish technical courses for mechanics. The Jewish Protectory and Aid Society bequest is for the relief of employees. The Hebrew Charities Building is to establish a library and to reduce the rent for the charitable societies occupying the building. The Educational Alliance is to devote its gift to work among women and children.

These bequests will be of inestimable value to the American chemists, and the undertakings in which the donor was so keenly interested during his lifetime will be firmly established and their success assured.

The technical press throughout the world deplored the loss of our distinguished colleague and paid tributes to his scientific attainments, his pleasing personality, his indefatigable energy in the interests of his fellow chemists, and his liberal support of plans for professional advancement. Our debt of gratitude has been perpetuated by his wise provisions, and the benefits of his bequests will have a lasting influence on the future of the chemical profession in America.

THE CODE OF ETHICS OF THE AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The Code of Ethics adopted by the Institute at its fifth annual meeting in Detroit is a work of unusual importance, and will have a far-reaching and beneficial influence on the chemical profession. In reading this code, which follows, it becomes apparent that

self-evident statements are made. We naturally think that every one is in agreement on these apparently self-evident statements, but, unfortunately, this is not always the case. Independent of the desirability, however, of formulating even these self-evident truths, there is a purpose back of the code which may be considered its key and which, if once seen, will explain the code and make its desirability apparent to every one. This purpose is to solidify, to draw together chemists in the recognition of a community of interests which, so far as the code goes, compliments and reinforces all individual interests. The indirect benefits which all chemists will derive by the promulgation and general observance by chemists of this code are of incalculable value. The code involves no limitation of this individuality, but adds to it something that will tend to make this same individuality more profitable and beneficial. The promulgation and adoption of this code is but a part of the broad movement which is receiving considerable emphasis in the business world in which it is recognized that ordinary competition should be supplemented by cooperation in order to be most effective and beneficial.

Without discussing in detail the various provisions of the code, we would point out that in line with the purpose back of the code it calls for a spirit of helpfulness, the upholding of the profession, the discouragement of sensationalism in estimates and public statements and the studious endeavor to give credit to others for their work. In other words, the code simply recognizes that the chemical profession depends for its success on the principle that the chemist does not live for himself alone. This principle of dependence applies to the relations between chemists and their relations with the public. We all know how dependent chemists are upon each other. If one wants evidence, let him refer to the tremendous amount of work published in our Abstract Journals from which we all draw benefits. The dependence of the chemist upon the public should be equally evident. The chemist should not do anything to weaken this dependence but rather should strengthen it. Everything that tends, as this code does, to strengthen the bonds of dependence between the public and the chemist will help the profession.

It is not to be expected that this code will revolutionize the chemical profession. It is, so to speak, a seed planted by the wayside which is sure to grow into something very much bigger—ultimately and inevitably bearing good fruit.

The committee, composed of G. W. Thompson, C. F. McKenna, A. C. Langmuir and A. D. Little, performed the delicate task entrusted to them with care and success. The final form as adopted by the Institute is as follows:

ARTICLE I.—PURPOSE OF THE CODE: To define the rules of professional conduct and ethics for the members of the Institute.

ARTICLE II.—THE INSTITUTE EXPECTS OF ITS MEMBERS:

1. That in all their relations, they shall be guided by the highest principles of honor.

2. The upholding before the public at all times of the dignity of the chemical profession generally and the reputation of the Institute, protecting its members from misrepresentation.

3. Personal helpfulness and fraternity between its members and toward the profession generally.

4. The avoidance and discouragement of sensationalism, exaggeration and unwarranted statements. In making the first publication concerning inventions or other chemical advances, they should be made through chemical societies and technical publications.

5. The refusal to undertake for compensation work which they believe will be unprofitable to clients without first advising said clients as to the improbability of successful results.

6. The upholding of the principle that unreasonably low charges for professional work tend toward inferior and unreliable work, especially if such charges are set at a low figure for advertising purposes.

7. The refusal to lend their names to any questionable enterprise.

8. Conservatism in all estimates, reports, testimony, etc., especially in connection with the promotion of business enterprises.

9. That they shall not engage in any occupation which is obviously contrary to law or public welfare.

10. When a chemical engineer undertakes for others work in connection with which he may make improvements, inventions, plans, designs or other records, he shall preferably enter into a written agreement regarding their ownership. In a case where an agreement is not made or does not cover a point at issue, the following rules shall apply:

a—If a chemical engineer uses information which is not common knowledge or public property, but which he obtains from a client or employer, any results in the form of plans, designs or other records shall not be regarded as his property, but the property of his client or employer.

b—If a chemical engineer uses only his own knowledge or information or data, which by prior publication or otherwise are public property, and obtains no chemical engineering data from a client or employer except performance specifications or routine information, then the results in the form of inventions, plans, designs or other records should be regarded as the property of the engineer, and the client or employer should be entitled to their use only in the case for which the engineer was retained.

c—All work and results accomplished by the chemical engineer in the form of inventions, plans, designs or other records, or outside of the field for which a client or employer has retained him, should be regarded as the chemical engineer's property.

d—When a chemical engineer participates in the building of apparatus from designs supplied him by a client, the designs remain the property of the client and should not be duplicated by the

engineer nor any one representing him for others without express permission.

c—Chemical engineering data or information which a chemical engineer obtains from his client or employer or which he creates as a result of such information must be considered confidential by the engineer; and while he is justified in using such data or information in his own practice as forming part of his professional experience, its publication without express permission is improper.

f—Designs, data, records and notes made by an employee and referring to his employer's work, should be regarded as his employer's property.

g—A client does not acquire any exclusive right to plans or apparatus made or constructed by a consulting chemical engineer except for the specific case for which they were made.

11. A chemical engineer cannot honorably accept compensation, financial or otherwise, from more than one interested party, without the consent of all parties; and whether consulting, designing, installing or operating, must not accept compensation directly or indirectly from parties dealing with his client or employer. When called upon to decide on the use of inventions, apparatus, processes, etc., in which he has a financial interest, he should make his status in the matter clearly understood before engagement.

12. The chemical engineer should endeavor at all times to give credit for work to those who, so far as his knowledge goes, are the real authors of such work.

13. Undignified, sensational or misleading advertising is not permitted.

14. Contracts made by chemical engineers should be subject to the Code of Ethics unless otherwise agreed.

ARTICLE III.—For the administration of this Code of Ethics, a Committee on Ethics shall be appointed by the president holding office at the time of the adoption of this Code with the approval of the Council, to consist of five members: one appointed for five years, another for four years, another for three years, another for two years, another for one year, and thereafter, the president then holding office shall appoint one member annually to serve for five years and also fill such vacancies as may occur for an unexpired term. All of these members shall be over forty years of age. The Committee shall elect its own chairman. The Committee on Ethics shall investigate all complaints submitted to them bearing upon the professional conduct of any member, and after a fair opportunity to be heard has been given to the member involved, shall report its findings to the Council, whose action shall be final.

ARTICLE IV.—AMENDMENTS: Additions to or modifications of this Code may be made according to Article VIII of the Constitution.

ELECTRICAL ENGINEERS' RESOLUTIONS REGARDING PATENT LEGISLATION

The American Institute of Electrical Engineers has formally adopted¹ resolutions bearing on im-

pending patent legislation and it is exceedingly gratifying to note that this organization has endorsed the policy so often recommended in THIS JOURNAL. The investigation of technical matters by a competent commission for the purpose of forming intelligent legislation might yield improved results on most any great problem, but it is particularly important that American patent law and practice be handled with care, skill and judgment and that its provisions be based upon scientific and economic considerations rather than upon political foundations.

The resolutions adopted by the Board of Directors of the Institute of Electrical Engineers are as follows:

WHEREAS, there are pending before the Congress numerous bills affecting and greatly modifying the Patent System in the United States, and

WHEREAS, the Patent System has been, and is, a tremendous factor in building up the present industrial prosperity of this country, thereby greatly contributing to the prosperity of the country as a whole, and

WHEREAS, any untoward change in the patent situation might disastrously affect this condition of industrial and general prosperity, and the conditions contributing to their continual augmentation, and

WHEREAS, in view of the intimate relation of the Patent System to the general welfare, no action looking toward any radical change in the Patent System should be taken without most careful consideration, and

WHEREAS, in our opinion, proper consideration of such important changes as are proposed can be had only by an unbiased, non-partisan commission, made up of men from various walks of life and not from any one vocation, or interest,

BE IT RESOLVED.—That the American Institute of Electrical Engineers, acting through its officers and Board of Directors, respectfully urge the Congress of the United States that they provide for a Commission, made up of unbiased, independent, non-partisan men of such national standing as will command the respect of the whole country; and chosen from different walks of life; and not more than one from any one calling or interest; and serving without pay. Such Commission to hold public hearings, and otherwise, as may appear to them best, to make a thorough and careful study of the American Patent situation, and to prepare and submit a comprehensive report and recommendations to Congress for such changes, if any, as may, as the result of their study, appear to them expedient, whether in the Patent Office, in the method of Court procedure, or in the organic Patent Law, and recommendations as to the Legislation they would propose for effecting said changes. And that we further respectfully urge that the Congress make ample provision for the expenses of said Commission, and

BE IT RESOLVED.—That we respectfully urge the Congress of the United States to hold in abeyance all proposed Legislation affecting the Patent System in whatsoever way until such time as the said Commission shall have had ample opportunity to hold the said hearings, and make the said study and report, and

BE IT FURTHER RESOLVED.—That these resolutions be printed and a copy be sent to each Senator and Representative of the United States who is a member of the Senate or House Committee on Patents.

MINERAL WASTE

The importance of the conservation of the mineral resources of the United States is again emphasized by the recent appearance of "Notes on Mineral Wastes," Bureau of Mines *Bulletin*, 47, by Charles L. Parsons, Mineral Technologist for the Bureau.

Wastes of fuels, the common metals, fertilizers, combined nitrogen, sulfur, arsenic, the rare earths; losses in the mining and treatment of ores and minerals; failure to make use of native ores; our need of potash, the platinum metals, new alloys and new uses for by-products of our present industries; any one of these is alarming. But there is encouragement in the reports of the recent advances in the metallurgy of iron; the desirable properties of the new alloys; the successful application of the electrical precipitation processes to all smoke and fume problems; the conservation made possible by the cement industries; the possible use of native feldspars and kaolins in the silicate industries; the recovery of combined nitrogen from coal, as well as the fixation of atmospheric nitrogen.

While a certain amount of waste is absolutely neces-

sary, we are reminded that our prodigal annual use and destruction of our natural resources must cease. Ages were necessary for their accumulation and they must be made to serve for the ages to come.

In his preface to this bulletin, Dr. Holmes points out that the present generation will not stint themselves nor will they tolerate financial loss of any kind in utilizing their resources for their ever-increasing needs. The rights and duties of the Federal Government are recognized "as being limited to the carrying on of inquiries and investigations with a view to determining the nature and extent of this waste of resources, the means by which it may be diminished, and the setting forth of the facts in the case." A more detailed report on this subject is promised as soon as the necessary research can be carried out.

It is our opinion that this work is the most important now being done by the government. No scientific society is in a position to support the researches necessary to disclose the "facts in the case." It should be the first duty of chemists and engineers, individually and collectively, to cooperate with the Bureau of Mines in this investigation. Judging from the preliminary report, the Bureau is attacking this problem on broad lines and with most excellent talent. Dr. Parsons' wide personal acquaintance in the profession will assure him of the helpful cooperation of all chemists in this gigantic undertaking.

ORIGINAL PAPERS

THE PRODUCTION OF CHLORINE SUBSTITUTION PRODUCTS OF METHANE FROM NATURAL GAS¹

By CHARLES BASKERVILLE AND H. S. RIEDERER²

The attempts which have been made to effect a chlorination of methane in order to obtain satisfactory yields of substitution products have been discussed in a previous publication.³ It may be noted here that while the formation of methyl chloride, dichloromethane, chloroform and carbon tetrachloride from methane has been experimentally shown by several investigators operating with various methods, and a number of processes have been patented for the production of these and other halogen derivatives of methane,⁴ so far no process has been worked on a commercial scale. Since there is an abundance of natural gas containing 50-90 per cent. methane in this country, the problem is of some importance—one which we thought would bear investigation along lines differing in certain respects from those hitherto followed.

In general, it may be said that the ultimate object of those studying the matter has been to produce

a constant yield of an intermediate product. Bearing in mind the demonstration of Phillips⁵ that the tendency of methane, when chlorinated, is to constantly produce either methyl chloride or carbon tetrachloride, it occurred to one of us (C. B.) that it would be more advantageous to obtain the end-product, from which, among other products, chloroform could be prepared by reduction. Accordingly a number of experiments were conducted with a view of devising a commercial process for the production of carbon tetrachloride from natural gas.

EXPERIMENTS WHEREIN A SPARK DISCHARGE WAS EMPLOYED

In preliminary experiments, an apparatus similar in principle to that used by Phillips was employed. It was finally decided, however, to construct an apparatus with a closed circuit, producing a circulation of the gases by heat on the rise, cooling on the drop, and recovering the products in a trap at the bottom; suitable openings being made in the apparatus for the introduction of chlorine and natural gas, and for the insertion of spark terminals in such a manner as to bring the spark in the junction line of the gases (Fig. I). Several modifications were made in this apparatus during the course of the experiments, and in the later experiments a horizontal reaction chamber (Fig. II), provided with a glass pocket for the collection of any condensation products in a liquid form

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² The authors have filed applications for patents on the novel features presented in this paper.

³ Baskerville and Hamor, *THIS JOURNAL*, 4, 216.

⁴ Mallet, U. S. Patent 220,397, October 7, 1879; Colin, U. S. Patent 427,744, May 13, 1890; Elworthy and Lance, French Patent 353,291, May 15, 1905; MacKaye, U. S. Patents 880,900, March 3, 1908, and 1,009,428, November 21, 1911; Walter, German Patent 222,919, November 5, 1909; and Pfeifer and Szaroasy, 12,058 D. Ann. P. 24,872, September 25, 1911.

⁵ *Am. Chem. J.*, 16, 362.

and with a hollow carbon terminal for the introduction of the natural gas,¹ was used. In the experiments wherein this form of reaction chamber was used, just

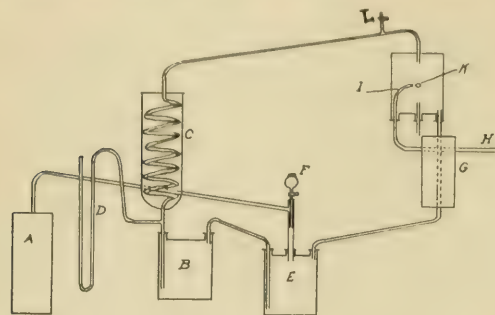


Fig. I

A, chlorine cylinder; B, receiver for substitution products of the reactions; C, condenser; D, pressure gauge; E, hydrochloric acid absorption chamber; F, funnel for introducing water; G, electric heater; H, tube for introducing natural gas, which plays between carbon spark terminals I; K; L, cock for releasing pressure.

as in the case of the original form of chamber, bridging between the carbon terminals invariably occurred, although combustion ensued almost immediately upon starting the spark. A very small yield of products was obtained.

The first three runs, using the original form of apparatus, showed that chlorine substitution products could be obtained, although the character of the products could not be determined owing to the small yields. The spark in these runs generally showed a dual character, partly resembling an arc and partly presenting the true color of a spark. Undoubtedly there were considerable ultra-violet rays in this latter portion.

In the runs, using the reaction chamber illustrated in Fig. II, the spark showed little of the deep blue and more of the flame. Since the gas was continuously directed into the spark, it burned continuously.

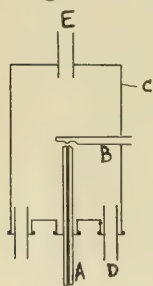


Fig. II

A, hollow carbon transmission tube for natural gas; this carbon is one terminal; B, solid graphite spark terminal; C, reaction chamber of glass; D, chlorine inlet; E, exit for gaseous products of reaction.

the modified apparatus, and it seemed reasonable to conclude that whatever chlorination was effected was through the agency of the ultraviolet rays and not by the combustion.

In all of the above experiments natural gas saturated with water was introduced into the circulating atmosphere of chlorine.

¹ Besides natural gas, methane, prepared by various methods, was used in preliminary experiments. In the following experiments, however, natural gas alone was used.

EXPERIMENTS WHEREIN ULTRA-VIOLET RAYS WERE UTILIZED

The apparatus used in the experiments which follow next was constructed as shown in Fig. III. The reaction chamber was a cruciform tube of glass, through two opposite components of which was inserted a quartz tube containing iron terminals.

In beginning, the apparatus was filled with chlorine, the heat and the spark started, and then natural gas (85 per cent. methane) was admitted. The pressure variations showed that a reaction occurred, but no product could be observed except a crystalline film suspended on the water in the receiving vessel. About 5 liters of natural gas were used. Even after continuing the run for 8 hours, during which time $3\frac{1}{2}$ liters of natural gas were used, no appreciable product was obtained. Accordingly, the apparatus was changed so that the natural gas was admitted below through the U-tube intended for a drain, causing it to bubble through the hydrochloric acid in the receiver.

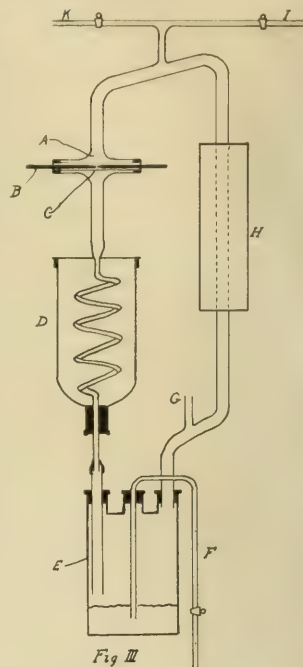


Fig. III

A, cruciform glass reaction viaduct; B, iron terminals; C, quartz tube containing iron terminals; D, condenser; E, receiver; F, syphon for emptying receiver; G, chlorine inlet; H, electric heater; I, natural gas inlet; K, connection to manometer.

In the next experiment, a considerable quantity of product collected in the receiving vessel: $7\frac{1}{2}$ liters of natural gas were used and the temperature of the heater was maintained so low that no vapors were observed in the rising tube above the furnace. After another run, in which $3\frac{1}{2}$ liters of natural gas were used, the apparatus was disconnected and the product was separated from the hydrochloric acid in the receiving vessel. Ten cc. of product were obtained; this was purified and fractionated. The first fraction came over at about 64°C ., and the fractions up to 76°C . were collected. A second fraction was then taken up to 88°C . and a residue remained in the fractionating bulb. The first and second fractions were colorless and clear, while the residuum possessed a yellow color. The first fraction amounted to about 75 per cent. of the total, the second and the residue to about 12.5 per cent. each. These experiments showed that approximately a 20 to 25 per cent. yield of carbon chlorides (chloroform and carbon tetrachloride) could be obtained from natural gas, using

a circulating atmosphere of chlorine in the apparatus described.

In the succeeding experiment the apparatus was made absolutely air-tight and a thermò-electric couple was introduced into the furnace to enable temperature readings. A run was made *without* a spark. Preliminary experiments showed that but a slight reaction occurred and that the crystalline product (hexachlorethane) formed was inappreciable, although very little natural gas was used; accordingly no further experiments were made without a spark with this apparatus.

In the following run, which lasted for 8 hours, considerable product collected, and the yield seemed to be in proportion to the natural gas used. The next runs were made after sweeping the apparatus with chlorine. After natural gas and chlorine were both added, the reaction proceeded smoothly and it was finally stopped by admitting chlorine alone. The product amounted to 14 cc. from about 10 liters of natural gas; this was purified and fractionated, and was found to consist of carbon tetrachloride and a small amount of chloroform and hexachlorethane.

For the next experiments, an outlet siphon for the hydrochloric acid produced and an inlet tube for natural gas were provided in the receiver. The apparatus was completely filled with chlorine, but no heat was used in the circuit. About 4 liters of natural gas were used in each run, and considerable product was obtained; the product was not separated, owing to the fact that it was in part distributed throughout the apparatus. It was determined that the product is very sparingly soluble in hydrochloric acid and chlorine water. Attempts were made to ascertain whether the ultraviolet rays have any influence on the reaction between chlorine and methane. Beginning with daylight, the ultraviolet source was then started and observations were made on the speed of the reaction. As in the preceding experiments, the issuing natural gas was saturated with water by passage through a water bottle. However, the variations in pressure were not sufficiently marked to lead one to infer that the ultraviolet rays have any effect on the reaction. In order to definitely establish this fact, a reaction chamber was constructed to accommodate an "Uviol" lamp to replace the spark section. Provisions were also made for exposing or not exposing the mixed gases to ultraviolet light, depending upon what was necessary to produce a reaction, for drying the gases by passage through sulfuric acid after the separation of the products of chlorination, and for passing the residual gases over quicklime. The form of apparatus used is shown in Fig. IV.

Beginning with a full charge of chlorine, the apparatus was run for one day and no appreciable reaction could be observed. From the experiments made, it seemed probable that the ultraviolet rays are not the necessary active rays required, for it was found that the reaction occurs in daylight, and the passage of the solar rays through glass would exclude ultraviolet light. From the observations made so far, it appeared that the solution of the problem was to find the proper rays.

Therefore, the "Uviol" lamp was removed and the aperture closed.

A tungsten filament lamp was mounted outside of the reaction chamber, surrounded by a reflector, and no appreciable reaction occurred, although runs were made under varying conditions. Using an incandescent gas mantle containing 10 per cent. of ceria, whereby the proportion of red rays was increased, with and without the aid of daylight, the reaction was practically *nil*, while with a mantle containing 3 per cent. of ceria only a slight reaction occurred. With the 3 per cent. ceria mantle, the reaction would take place when daylight was admitted, but would practically cease in the dark. At times a slight reaction was noted when working in the dark, but this was attributed to diffused light entering through the laboratory door. Dark here means the exclusion of daylight.

In the next series of experiments a projection lantern, using only one condenser lens and ordinary carbons was placed in such a position as to light the upper section of the reaction chamber. The lantern was run on an 8 ampere 235 volt current, and it was shown conclusively that the arc light cause the reaction

to take place. Colored screens were then interposed between the lantern and the reaction chamber, and in this manner the rays favoring the reaction were determined. A spectroscopic examination of the screens (solutions of coal tar dyes, blue, green, red and yellow, such as are used in the Pinotype color-photography outfit) showed that the blue screen passed through the green and gave but a dim indication in the deep red; that the green cut out every ray except the green with a blue fringe; and that the yellow and red screens

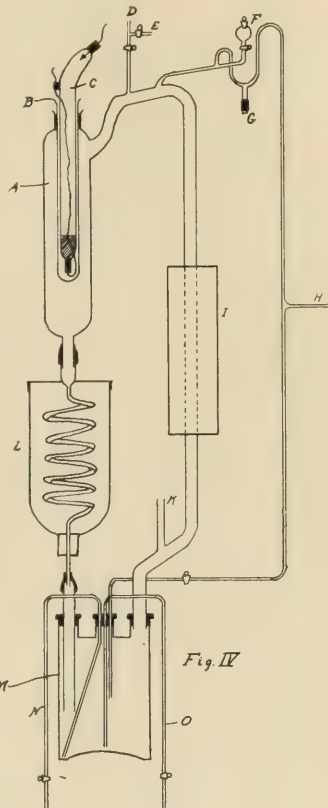


Fig. IV
A, reaction chamber of glass; B, large thin-walled quartz tube; C, Uviol lamp inserted after current is started; D, tube connection to manometer; E, cock for releasing pressure; F, funnel for introducing water; G, trap; H, tube for introducing natural gas before or after the heater; I; K, chlorine inlet; L, condenser; M, receiver; N, siphon for removing heavy products of reaction; O, siphon for removing water solution of hydrogen chloride produced in the reactions.

excluded the blue end of the spectrum along with part of the green. A number of experiments demonstrated that the unscreened arc light and the arc light screened with the blue allowed a good reaction speed, while the interposition of the green, yellow and red screens slowed down the reaction almost immediately and to a considerable degree; on replacing the blue screen, however, the reaction was at once accelerated. It was found that it made little difference whether chlorine or natural gas was being run into the apparatus, except that the character of the product varied accordingly. Further experiments showed that the blue end of the spectrum is the active agent for the reaction of chlorine and natural gas. It was found that screening is of little use, since the inactive red, yellow and green rays are hardly of an interfering character. The primarily important condition was found to be a source of light rich in the rays of the visible blue spectrum—that is, the spectrum from the bluish green through the visible violet. We have found that the invisible spectrum (the ultra-violet) does not induce the desired activity and that it plays little part in the reaction.

As it was not always convenient to fuse the large glass tubes in making connections, it may be of interest to give the method resorted to for making tight junctions through which such corrosive gases as chlorine and hydrogen chloride may be passed. The glass tubes were first cut smooth and closely fitted to each other. The junction was then wrapped with wet, thin sheets of asbestos paper. After drying, the asbestos was given several coats of Bakelite varnish No. 4. The next day this was tightly wrapped with electric adhesive tape and thoroughly coated again several times with the Bakelite varnish.

DEPARTMENT OF CHEMISTRY
COLLEGE OF THE CITY OF NEW YORK

APPLICATIONS OF DUCTILE TUNGSTEN¹

By C. G. FINK

Less than ten years ago tungsten was universally conceded to be a very brittle metal. Since the introduction of ductile tungsten,² however, large quantities of drawn wire, flexible and strong, are being daily produced for the manufacture of incandescent lamps.

We have studied the physical and chemical properties of this new tungsten, and have obtained a number of very interesting results.

The ductile metal is practically insoluble in all of the common acids,³ its melting point is higher than that of any other metal,⁴ its tensile strength exceeds that of iron and nickel, it is non-magnetic, it can be drawn down to smaller sizes than any other metal, and its specific gravity is 70 per cent. higher than that of lead.

It was natural that a metal with such striking properties as these should soon find applications other than that for incandescent lamps.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² C. G. Fink, *Trans. Am. Electrochem. Soc.*, **17**, 229; W. D. Coolidge, *Trans. Am. Elec. Inst. Eng.*, **29**, 961.

³ W. E. Ruder, *Jour. Am. Chem. Soc.*, **1912**, 387.

⁴ I. Langmuir, *Trans. Am. Electrochem. Soc.*, **20**, 237.

ELECTRICAL CONTACTS

Wrought tungsten has been substituted with success for platinum and platinum-iridium as contact points in spark coils, voltage regulators, telegraph relays, etc.¹ The service far exceeds that for platinum and platinum-iridium contacts due to the greater hardness, higher heat conductivity and lower vapor pressure of tungsten as compared with platinum.

TUNGSTEN FURNACES

These furnaces are of two types. The type recently described by Winne and Dantsizen² consists of an aluminum tube wound with tungsten (or molybdenum) wire. To prevent oxidation the tube is encased in an air-tight box with an inlet and outlet for hydrogen. This furnace is admirably well suited for laboratory experiments. Temperatures of 1600°–1800° C. can be easily maintained for hours, whereas platinum at these temperatures would rapidly disintegrate.

A second type of tungsten furnace³ is constructed on lines similar to those of the Arsem vacuum furnace. A tungsten metal tube takes the place of the helical carbon resistor. The tube is surrounded by a screen and the whole enclosed in an air-tight compartment almost identical to that used by Arsem. The compartment is either evacuated or a small quantity of gas, such as hydrogen, is introduced. This furnace lends itself admirably for the study of reactions at very high temperatures, such as the production of artificial gems.

TUNGSTEN GAUZE

We have used this gauze successfully for separating solids from acid liquors. We performed these experiments on a laboratory scale. However, this gauze could well be used on a commercial scale. For example, for the removal of sludge from copper refining baths, and for centrifugal apparatus, in general, whenever acid liquids or acid gases are dealt with.

Furthermore, it might be used in apparatus such as described by Cottrell⁴ for the removal of sulfuric mist from gases. The Cottrell electrodes consist of three concentric cylindrical screens of iron wire, the inner and outer ones acting as discharge electrodes while the intermediate screen and the outer leaded glass containing vessel act as collecting electrodes from which the deposited acid drains into a leaden pan below. Tungsten gauze is not attacked by sulfuric acid and would consequently give a much longer life than iron gauze.

WROUGHT TUNGSTEN TARGETS FOR ROËNTGEN TUBES

This application has proved to be one of the most interesting. Tungsten is very well suited for targets or anticathodes and the realms of application and efficiency of the Roëntgen tube have been thereby greatly increased.

As has been shown by Coolidge, the high specific gravity, high melting point, high heat conductivity and low vapor pressure make tungsten a far more efficient target than any other metal.

¹ W. D. Coolidge, *Trans. Am. Inst. Elec. Eng.*, **31**, 870; *THIS JOURNAL*, **4**, 2.

² *Trans. Am. Electrochem. Soc.*, **20**, 287.

³ U. S. Pat., 1,006,620.

⁴ *THIS JOURNAL*, **3**, 542.

THERMOCOUPLES

We are investigating the thermoelectric properties of the couple, tungsten-molybdenum. The electromotive force increases with the temperature up to about 540° then decreases and passes through zero millivolt at about 1300°. We have found this couple very convenient for high temperature measurements in the tungsten-hydrogen furnace.

STANDARD WEIGHTS

A material suitable for standard weights must preferably be hard yet plastic, it must not be easily scratched nor marred, but still not be so hard that it will chip or break; furthermore, it must withstand the action of the atmosphere and finally it must be small in bulk. Now wrought tungsten can be made so hard that it will readily scratch glass and still be ductile; furthermore, the density is high (19.3 to 21.4) and it is unaffected by the atmosphere. Tungsten weights remain wonderfully constant.

TUNGSTEN CELLS

We have taken up the study of the electrochemical behavior of tungsten and have made up a series of cells and combinations. All measurements were made at 25° and compared with the calomel electrode as standard. Our readings for the cell tungsten, aqueous sodium hydrate, potassium chloride, calomel, mercury are:

5 N NaOH, 0.68; 2 N, 0.62; N, 0.57; $\frac{1}{2}$ N, 0.525; $\frac{1}{10}$ N, 0.50; $\frac{1}{20}$ N, 0.48; $\frac{1}{40}$ N, 0.455; $\frac{1}{100}$ N, 0.445; $\frac{1}{320}$ N, 0.380; and 0.0 N, 0.06 volt. In the last cell the tungsten rod was immersed in distilled water.

The addition of small amounts of impurities to the tungsten metal causes the tungsten—sodium hydrate electrode to assume E. M. F. values that approach that of zinc in zinc sulfate.

The values for potassium hydrate are similar to those for sodium hydrate. The E. M. F. of the cell $\text{Hg}-\text{Hg}_2\text{W}_{11} + \text{Na}_2\text{WO}_4 \text{ solid}-\text{Na}_2\text{WO}_4 \text{ sat. soln.}-\text{solid Na}_2\text{WO}_4-\text{W}$ was found to be 0.505 volt and promises to be a good standard cell.

MISCELLANEOUS APPLICATIONS

Besides the applications of tungsten cited above, many others have been but partly worked out and others merely suggested.

Owing to its chemical stability the finest sizes of wire down to 0.0002" or 0.005 mm. in diameter are well adapted for galvanometer suspensions and for cross hairs in telescopes. It has also been suggested to use these fine wires in surgical operations in place of the coarser gold and silver wires. A further suggestion is the use of the wire in musical instruments. The tensile strength and elasticity of tungsten wire are exceptionally high (see table below).

It could be used to advantage in climates where steel is readily corroded.

We are investigating the formation of hydrocyanic acid gas by passing over heated tungsten wire mixtures of nitrogen and acetylene or methane.¹

The heat of formation of HCN is: $\text{C}_2\text{H}_2 + \text{N}_2 = 2\text{HCN} - 9400 \text{ cal.}^1$

We are making acid-proof dishes and tubes out of tungsten. Furthermore, tungsten wire recommends itself as a unit resistance since it can be made absolutely pure, can be easily duplicated and is not corroded.

Since tungsten is non-magnetic and elastic it is being tried out in electrical meters, replacing the phosphor-bronze springs.

Similarly watch springs could be made which would never become magnetized. Finally we might mention: tungsten pen points, tungsten drawing dies, tungsten knife blades, tungsten reinforced asbestos curtains and fire-proof coverings, etc.

TABLE OF PHYSICAL AND CHEMICAL PROPERTIES OF DUCTILE TUNGSTEN

Density, 19.3 to 21.4
Tensile strength, 322 to 427 kg. per sq. mm.
Young's modulus of elasticity, 42,200 kilograms per square mm. (steel 20,000): i. e., twice as elastic as steel.
Melting point, 3177 (Langmuir) 3100 \pm . 60 (v. Pirani & Meyer).
Boiling point, 3700° (?).
Thermal conductivity, 0.35 gram cal. per cm. per sec. per 1° (Pt, 0.166) (calculated, see foot-note 1, column 2, p. 8).
Expansion coefficient, 4.3×10^{-6} (Pt, 8.8×10^{-6}).
Specific heat, 0.0358 (Weiss).
Resistivity (25°) hard: 6.2 microhms per cu. cm.; annealed: 5.0 microhm per cu. cm.
Temperature coefficient of resistance, 0.0051 (0°-170°).
Hardness, 4.5 to 8.0 (Mohs scale).
Insoluble in HCl, H_2SO_4 , HNO_3 , HF, NaOH, KOH, (aq.) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4$ (see foot-note 2, column 1, p. 8). Soluble in mixtures of HF and HNO_3 and in fused nitrates, nitrites and peroxides.
The boiling point of the metal has not yet been determined.
The Young's Modulus of Elasticity we determined with a wire 0.00648 cm. in diameter and 784.86 cm. long. The smallest weight (P) was 250 and the largest 1125 grams. The elastic elongation was 0.35 cm. for the smallest weight and 1.65 cm. for the largest. The average for five different weights was 42,200.
The hardness values were determined with the scleroscope and the values translated into the Mohs scale.
GENERAL ELECTRIC CO.
NEWARK, N. J.

BLUE GELATINE COPPER²

By WILDER D. BANCROFT AND T. R. BRIGGS

Copper and the copper alloys such as brass and the bronzes lend themselves very readily to artistic decoration by means of colored superficial films or "patinas." Great as is the variety of colors which may thus be imparted to copper, nevertheless a rich and true blue patina for this metal is practically unknown. It was while seeking such a blue surface film that the electrolysis of copper acetate solutions containing gelatine was first performed. One gram of gelatine was dissolved in 325 cc. of a 1 per cent. solution of cupric acetate and this mixture electrolyzed between carefully cleaned and burnished electrodes of sheet-copper. The electrolysis was continued for five minutes at a cathode (and anode) current density which varied between 0.15 and 0.45 amp/dm². The process was carried out at room temperature.

The electrolysis performed, the cathode was found to be covered on its inner surface with a thin, pale brown deposit, which, when rubbed with the fingers, was seen to possess a peculiar, slippery surface caused by a very appreciable amount of gelatine deposited simultaneously with the metallic copper. No gas

¹ Wartenburg, Z. f. anorg. Chem., 82, 299.

² Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

¹ Compare Berthelot and Lipinski, Z. Elektrochemie, 17, 287.

became visible at either pole during the passage of the current.

In itself, this pale brown cathode deposit gave no indication of its peculiar properties and it was by chance only that these were discovered. An electrode, freshly coated with a layer of the gelatine-copper, was by an oversight allowed to remain in the solution of copper acetate from which the film of metal had just been deposited and the current was turned off. On removing the electrode from the solution, it was noticed that the brown color originally possessed by the cathode film had given place to a purplish blue of extraordinary brilliance and beauty. This led to further experiments.

A second electrode was then coated with a film of gelatine-copper and, after careful rinsing with cold tap water, immersed in a 5 per cent. solution of copper acetate containing no gelatine. Straightway there ensued a remarkable series of color changes upon the surface of the copper deposit; hues of startling evenness and intensity followed each other in regular succession until the electrodes had acquired a magnificent deep-blue coloration. This process we shall speak of as a "development," since it bears a certain resemblance to the development of the silver image in the process of photography.

EXPERIMENTAL

1. *Effect of Gelatine.*—After the process of development had been discovered, a more systematic study of the formation and nature of gelatine-copper was undertaken. It then became evident that gelatine must be present in the electrolyte and that this colloid exerted a tremendous influence upon the nature of the cathode deposit. The term "gelatine-copper" was thus justified. The optimum gelatine concentration was found to lie between 0.25 and 0.66 per cent. The electrolysis of copper acetate solutions containing no gelatine failed to give the developable films nor was it possible to substitute other hydrophilic colloids such as starch or gum-arabic for gelatine or glue.

2. *Nature of Electrolyte.*—Electrolysis of copper formate, acetate, and propionate solutions containing gelatine resulted in cathode films which developed blue in copper acetate although this development was imperfect in the case of the deposits from the formate solution. Copper sulfate solutions of different strengths and varying gelatine content failed absolutely to give developable deposits. Similar results were obtained with solutions of copper nitrate and chloride.

3. *Effect of Temperature.*—Variation of the temperature at which the electrolysis was performed led to interesting results. Between 20° and 40° C., the cathode deposit was of the usual pale brown color and gave a more or less satisfactory color-development to blue in copper acetate. At 50° C. or at higher temperatures, the cathode deposit was colored a bright red or a brick-red and was unaffected by the developing solution. Between 55° and 60° a short electrolysis with a low current density gave a gold-colored but very thin film which had a rather iridescent appearance. These gold and red films can be lacquered with com-

plete success and are interesting in their application to metalochromy.

4. *Other Factors.*—The best results were obtained with copper acetate or propionate solutions made up in the proportion of 1 or 2 parts by weight of the crystallized salt to 100 parts of water. The electrolyte should be neutral or at most but very slightly acid. The current density must be low—between 0.15 and 0.45 amp./dm²—and the process need not exceed 5 minutes in duration. The nature of the metal used as cathode is of little importance as long as the copper solution is not decomposed. Thus with nickel, brass, and platinum, good deposits were obtained as adherent cathode films which developed a good blue color.

5. *The Development of the Blue Color.*—A 5 per cent. copper acetate solution containing no gelatine was used as the developing bath throughout this work, although a copper propionate solution may also be employed. Copper formate developer gave less satisfactory results. A large number of other salt solutions were then tried as developers with practically no success. Thus in normal copper sulfate solution a film of gelatine-copper was colored a dull dark indigo. In *N/50* copper sulfate a fairly good blue color was developed although the colors obtained with sulfate solutions are distinctly inferior to those prepared with acetate developer. Very dilute copper nitrate oxidized the film to dark brown copper oxide while a chloride solution spoiled the deposit entirely.

Several oxidizing solutions were next used with negative results. Potassium chromate, bichromate, permanganate, perchlorate, chlorate, and persulfate failed to give even a trace of blue coloration. The films were usually oxidized slowly to brown cupric oxide. Reducing solutions gave no development. The film of gelatine-copper was unaffected by dilute, warm, hydrazine hydrate and underwent accelerated blue development in copper acetate after such treatment.

A solution of sodium acetate gave no blue coloration of the copper film nor was it otherwise with the acetate solutions of other metals. Hence this phenomenon must be a function of the copper contained in the developing solutions.

6. *Reverse Development.*—An electrode, covered with a deep blue film, was immersed in a very dilute aqueous solution of hydrazine hydrate and, in a short time, bubbles of nitrogen began to form on the blue surface. The blue color then slowly faded away, until, passing in the reverse direction through the series of colors previously described, the film of gelatine-copper again took on its original brown color. This process was called a "reverse development."

The reverse development completed, the electrode was rinsed in distilled water and once more immersed in the usual copper acetate developer. The blue color formed again quickly, but was a bit thin and uneven.

If a film of gelatine-copper is allowed to stand undeveloped for several hours, it completely loses its power of developing in copper acetate. This is probably due to its oxidation by the air because it was

found that treatment of such a "dead" film with hydrazine hydrate was sufficient to regenerate its powers of development. The same result was obtained with a film after immersion in warm, dilute hydrogen peroxide—no development occurred until the layer of oxide so produced had been reduced with hydrazine.

THEORY AND CONCLUSIONS

Schützenberger, by the electrolysis of copper acetate solutions, obtained at the cathode a peculiar form of copper; and, being unable to explain its unusual behavior, he announced it as an allotropic modification. Wiedemann incorrectly contended that the new form of copper was really the oxide of that metal, while recently Benedicks has advanced the idea that we have to deal with a solid solution of acetic acid in copper. It can be shown, however, by a careful study of their results by, and consideration of, the facts of colloid chemistry, that the allotropic copper of Schützenberger is merely the normal metal in the form of an irreversible colloid gel.

The same conclusion is applicable to the deposits of gelatine-copper described in this paper. The gelatine acts here as the "protecting colloid," migrates by cataphoresis to the cathode, and there inhibits the growth or crystallization of the copper nuclei. Gelatine-copper is an irreversible gel of colloidal copper. The whole phenomenon is but another example of the marked influence of organic and other colloidal substances upon metals prepared by electrolysis, accounts of which have appeared in the recent papers of Müller and Bahntje, Snowdon and others.

What is the nature and mechanism of the process of the color development? This is indeed a difficult problem, chiefly because of the exceeding small quantities of reacting material of necessity dealt with. The blue, although a superficial color, is nevertheless not the color of a thin film of gelatine or oxide bringing about interference disturbances in the reflected rays of light. Nor does it seem to be the color of a definite chemical compound. The blue layer does contain oxide as is shown by its action with hydrazine and yet it cannot be prepared by any process of simple oxidation. It cannot be produced by the partial coagulation of the copper gel.

It was shown by Wiedemann that Schützenberger's copper possesses the power of adsorbing very considerable quantities of copper oxide from copper acetate solutions. This observation furnished the clue to the process of development. The color changes that appear upon the film are the result of a *surface adsorption of hydrous copper oxide from the copper solution*. The hydrous copper oxide is present as a suspension in very appreciable quantities in the acetate or propionate solutions, being the product of hydrolytic dissociation. This being the case, we should expect the best development with the acetate solutions and but little color effect with the sulfate and chloride developers.

The reversal of development caused by hydrazine is due to the reduction of the adsorbed oxide. There seems to be a certain definite concentration of oxide

in the copper film necessary for the production of a blue color. As the concentration of the oxide increases by continued adsorption, the film passes through the series of colors so distinctive of the development.

In conclusion it can be said in support of this hypothesis that it is in accord with many of the established facts in colloid chemistry and explains in the best possible manner this decidedly obscure phenomenon. Stannic oxide adsorbs gold from suspension and forms the "Purple of Cassius;" under very special conditions colloidal copper adsorbs hydrous copper oxide and similarly gives an intensely colored adsorption compound.

SUMMARY

The electrolytic production of a form of colloidal copper was performed with certain copper solutions containing gelatine.

This new form of copper develops a remarkable series of colors when immersed in certain copper solutions, a peacock-blue being the finest color obtained.

The process of development is an adsorption of hydrous copper oxide by the surface of the colloid film.

There have been described methods of coloring metal objects gold, golden brown or red.

CORNELL UNIVERSITY
ITHACA, NEW YORK

THE CLASSIFICATION OF BITUMINOUS AND RESINOUS SUBSTANCES¹

By HERBERT ABRAHAM

The terms bitumen, asphalt, resin, tar, pitch, etc., are in common use, yet it is surprising to note how inadequately they are defined in most of the standard works and text-books. This may be explained by the fact that these words originally had limited meanings, but in keeping pace with the progress of science they were extended in scope until they completely outgrew their original bounds.

It is probable that each of the expressions at first pertained to the aggregate properties characteristic of some typical substance closely associated with the processes of daily life. Thus, the generic term "resin" originated in the word "rosin," and it even now alludes to substances resembling ordinary rosin in appearance and physical properties. Similarly our comprehension of the generic term "wax" is based largely on the physical characteristics of the oldest known wax; namely, common beeswax.

From time to time, as new substances were discovered in nature, or produced in the arts, the meanings of these words were arbitrarily extended to include them. This resulted in a certain amount of overlapping and consequent confusion. As the chemistry of these substances was investigated, this was in certain cases adopted as an additional means of differentiation. But we are still forced to rely principally upon the physical characteristics of these groups of materials, for even to-day comparatively little accurate information is available with respect to their chemical composition. It is probable, however,

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

that in the future this latter will be adopted as a basis of nomenclature.

The complexity of these terms and the existing confusion becomes especially apparent in attempting to define and limit the scope of claims in letters patent. We are not infrequently confronted with this problem in patent controversies, owing to the relatively large number of patents classified under the heading of "Plastic Compositions," and involving the use of asphalts, pitches and the like.

The object of this paper is to submit a list of definitions and a system of classification gradually evolved by the author while engaged in "patent causes." In this connection, it might be stated that several of these definitions (*e. g.*, resin, bitumen, resinous substance and bituminous substance) have already been accepted by the courts in this country. The author hopes, therefore, that at least some of his findings may be of value to the committee now engaged in fixing the nomenclature of bitumens.

The definitions which will follow have been based on one or more of the following items:

I. Origin.

- | | |
|------------|-----------------------------|
| 1. Natural | 2. Artificial—Obtained from |
| Mineral | Distillation processes |
| Vegetable | Oxidation processes |
| Animal | Sulfurization processes |
| | 3. Variable. |

II. Composition.

In such cases where this is known with certainty.

III. Solubility.

In water

In carbon disulfide, benzol, etc.

IV. Physical Properties.

- | | |
|------------------|---------------------------|
| 1. Hardness | 5. Lustre |
| Liquid | Waxy |
| Viscous | Resinous. |
| Semi solid | 6. Feel: |
| Solid. | Adherent |
| 2. Color in Mass | Non-adherent |
| Light | Unctuous. |
| Dark. | 7. Odor: |
| 3. Structure | Tarry, etc. |
| Amorphous. | 8. Behavior towards Heat: |
| 4. Fracture | Fusible |
| Conchoidal | Difficultly fusible |
| Hackly. | Infusible. |

DEFINITIONS

Bitumen.—A naturally occurring² hydrocarbon complex,⁷ often associated with a mineral matrix,⁸ insoluble in water,¹¹ but largely soluble in carbon disulfide, benzol, etc.¹³ Its color²⁴ and hardness²¹ are variable.

Pyro Bitumen.—A dark colored,²³ solid,²⁴ infusible,³⁵ naturally occurring² hydrocarbon complex,⁷ often associated with a mineral matrix,⁸ insoluble in water,¹¹ and relatively insoluble in carbon disulfide, benzol, etc.¹⁴

Bituminous Substance.—A term applied to (a) substances containing bitumens or pyro bitumens. (b) Substances resembling either the viscous or solid¹⁷ bitumens, or pyro bitumens¹⁸ in their solubility and physical properties, *i. e.*, having an amorphous structure²⁵ and dark color in mass.²³

Maltha.—A dark colored²³ and viscous,¹⁵ naturally

occurring² hydrocarbon complex,⁷ insoluble in water,¹¹ but completely soluble in carbon disulfide, benzol, etc.¹⁴

Asphalt(um).—A dark colored,²³ and more or less viscous to solid¹⁷ hydrocarbon complex,⁷ including: (a) The easily fusible bitumens¹³ often associated with a mineral matrix,⁸ not having a "waxy" lustre²⁷ or unctuous feel.³⁰ (b) Fusible residuums obtained from the distillation,³ oxidation,⁴ sulfurization,⁵ etc., of bitumens.

Asphaltite.—A dark colored,²³ solid,³⁰ difficultly fusible,³⁴ naturally occurring² hydrocarbon complex,⁷ insoluble in water,¹¹ but more or less completely soluble in carbon disulfide, benzol, etc.¹³

True Resin.—A term applied to various vegetable principles occurring in, or obtained from, the secretions or saps of certain plants and trees.¹ They are hard, fusible³³ and more or less brittle, non-adherent to slightly adherent²⁹ solids at ordinary temperatures,²⁰ usually light colored in mass,²² having an amorphous structure,²⁵ conchoidal fracture²⁶ and "resinous" lustre.²⁸ They are insoluble in water,¹¹ but more or less completely soluble in carbon disulfide, benzol, etc.¹³ They are oxidation or polymerization products of the terpenes, and generally contain "resin" acids and esters.

Resinous Substance.—A term applied to (a) substances containing true resins. (b) Substances of variable origin⁶ and composition¹⁰ resembling true resins in their physical properties (with the exception of color), and solubility (*vide* true resins).

Mineral Resin.—A term applied to the solid bitumens (*vide* bitumen).

Oleo Resin.—The viscous to semi-solid²⁶ and usually light colored solutions of true resins in essential oils,⁹ either obtained from, or constituting, the saps of certain plants and trees.

Gum Resin.—The semi-solid¹⁹ to solid and usually light colored²² emulsion or mixtures of true resins with various gums (carbohydrates), constituting the sap of certain plants and trees, partly soluble in water.¹²

Tar.—A dark colored,²³ bituminous substance, liquid or semi-liquid at room temperature, often possessing a characteristic "tarry" odor,³¹ usually insoluble in water,¹¹ but miscible with carbon disulfide, benzol,¹³ etc.,¹³ and which on distillation, oxidation, etc., forms a pitch. Its composition¹⁰ and origin⁶ are variable.

Pitch.—A dark colored,²³ fusible³³ and more or less viscous to solid¹⁷ bituminous or resinous substance, insoluble in water¹¹ but more or less completely soluble in carbon disulfide, benzol, etc.¹³ Its composition¹⁰ and origin⁶ are variable.

Wax.—A term applied to unctuous,³⁰ fusible³³ and more or less viscous to solid¹⁷ substances, having a characteristic "waxy" lustre,²⁷ and which are insoluble in water,¹¹ but more or less soluble in carbon disulfide, benzol, etc.¹³ They are extremely susceptible to changes in temperature.³² Their composition,¹⁰ origin⁶ and color²⁴ are variable.

The terms "resinous substances" and "bituminous substances" overlap, as it were, for both of them include mineral waxes, asphaltum and asphaltites

This is made clear by the following table:

RELATION BETWEEN BITUMINOUS AND RESINOUS SUBSTANCES		ORIGIN	
		BITUMINOUS SUBSTANCES	RESINOUS SUBSTANCES
NATURAL	Bitumens	Natural Gas	True Resins Oleo Resins Gum Resins
		Petroleum	
		Mineral Wax	
		Asphaltum	Vegetable Resins
NATURAL	Pyro Bitumens	Asphaltum	
		Asphaltites	Mineral Resins
		Peat	
		Lignite	
ARTIFICIAL	Artificial Mixtures	Bituminous Coal	Pitches
		Anthracite Coal	
		Metamorphosed Asphalts	
		Tars	Artificial Mixtures Synthetic Products Oxidized Oils
		Pitches	

Pyro bitumens, asphalts, tars, pitches and waxes admit being classified according to their origin as follows:

Pyro Bitumens.—(a) Derived from the metamorphosis of vegetable growth (e. g., peat, lignite, bituminous coal and anthracite coal).

(b) Derived from the metamorphosis of asphalts (e. g., elaterite or wurtzilite, albertite and impsomite).

The distinguishing features of the pyro bitumens derived from the metamorphosis of asphalts are as follows:

DISTINGUISHING FEATURES OF PYRO BITUMENS DERIVED FROM ASPHALTS

	STREAK	SP. GR. AT 77° F.	MELTING PT. K. & S. method	FIXED CARBON Percentage	FRACTURE	LUSTRE	IN FLAME
<i>Elaterite (Wurtzilite)</i>	Light brown	1.05-1.07	Decomposes	5 to 25	Conchoidal	Bright	Softens and burns
					Hackly	Fairly bright	Softens and burns
<i>Albertite</i>	Black	1.07-1.10	Decomposes	25 to 50	Conchoidal	Bright	Intumesces
					Hackly	Dull	Intumesces
<i>Impsomite</i>	Black	1.10-1.20	Decomposes	50 to 57	Hackly	Dull	Decrepitates

Asphaltum.—(a) Natural—Resulting from a slow natural process of metamorphosis, known as natural asphalts ("mineral pitches").

1. Occurring in a fairly pure state.

2. Associated with a mineral matrix (e. g., calcareous, siliceous or earthy).

(b) Artificial—Resulting from the distillation, oxidation, etc., of mineral oils: known as petroleum asphalt ("petroleum pitches").

1. Straight petroleum asphalt.

2. Cut back.

3. Blown (oxidized), petroleum asphalt.

4. Dubb's (sulfurized) petroleum asphalt.

Asphaltites.—The distinguishing features of the individual asphaltites are as follows:

DISTINGUISHING FEATURES OF THE INDIVIDUAL ASPHALTITES

	STREAK	SP. GR. AT 77° F.	MELTING PT. K. & S. method	FIXED CARBON Percentage	FRACTURE	LUSTRE	IN FLAME
<i>Gilsonite (Uintaite)</i>	Brown	1.06-1.10	250-350° F.	10 to 20	Conchoidal	Bright	Softens and flows
					Hackly	Fairly bright	Softens and flows
<i>Glance pitch</i>	Brown to black	1.10-1.25	250-350° F.	20 to 30	Conchoidal	Bright	Variable
					Hackly	Fairly bright	Variable
<i>Manjak</i>	Black	1.15-1.175	350-450° F.	30 to 40	Conchoidal	Bright	Softens, splits and burns
					Hackly	Fairly bright to dull	Softens, splits and burns
<i>Grahamite</i>	Black	1.175-1.20	450-550° F.	40 to 50	Conchoidal	Bright	Decrepitates violently
					Hackly	Fairly bright to dull	Softens, splits and burns

Tar.—(a) Natural—(e. g., mineral tars or maltha).

(b) Artificial—The soft residues obtained.

1. From the distillation of petroleum (e. g., petroleum tar or soft petroleum asphalt).

2. From the destructive distillation of organic substances and pyro bitumens; (e. g., pine tar, wood tar, bone tar, coal tar, mineral tar (maltha), petroleum tar, etc.).

Pitch.—(a) Natural—Resulting from a slow natural process of metamorphosis known as "mineral pitches" or natural asphalts; e. g., Trinidad pitch, glance pitch, gilsonite, etc.

(b) Artificial—

1. Residues from the distillation, oxidation, etc., of mineral oils; e. g., petroleum pitch, blown petroleum asphalt, sludge pitch, Dubb's asphalt, etc.

2. Residues from the distillation of tars; e. g., coal-tar pitch, brown-coal-tar pitch, coke-oven-tar pitch, blast-furnace-tar pitch, water-gas-tar pitch, generator-gas-tar pitch, wood-tar pitch, pine-tar pitch, etc.

3. Residues from the distillation of fusible organic substances, the process having been terminated before the actual formation of coke; e. g., resin pitch, stearin pitch (fatty acid pitches), etc.

4. Artificial mixtures complying with the above general definition of the term "pitch," regardless of their origin or composition (e. g., insulating pitch, Brewer's pitch, roofing pitch, etc.).

Wax.—(a) Natural—

1. Mineral (e. g., ozokerite, ceresine, montan wax, hatchettite, etc.).

2. Vegetable (e. g., Japan wax, carnauba wax, etc.).

3. Animal (e. g., beeswax, spermaceti, etc.).

(b) Artificial—

1. From the distillation of paraffinaceous petroleum, ozokerite, etc.

2. From the destructive distillation of lignite (brown coal), paraffinaceous shales, etc.

TERMS USED IN PRECEDING DEFINITIONS

¹ Vegetable: These may be of recent formation or ancient formation. In the latter case, they are termed "fossil." It is usually conceded, however, that in either event they are of vegetable origin.

² Naturally Occurring: This excludes artificial products, as for example, certain tars and pitches, synthetic products, artificial mixtures, etc.

BITUMINOUS SUBSTANCES

RESINOUS SUBSTANCES

NATURAL		ARTIFICIAL	
BITUMENS	Gaseous	PYRO-BITUMENS	TRUE RESINS
	Natural gas		Common Resins
	Marsh gas		Fossil Resins
	Liquid or Semi Liquid		Common Turpentine
Solid	Petroleums	Solid	Canada Balsam
	Asphaltic base		Venice Turpentine
	Mixed		Burgundy Pitch
	Matthas ("mineral tar")		Ammoniacum
Occur fairly pure	Mineral waxes	Mineral matter predominates	Asafoetida
	Ozokerite (ceresine)		Bdellium
	Montan wax		Gamboge
	Hatchettite		Myrrh
Mineral pitches	Asphalt(um)	Bone tar and bone-tar pitch	Ozokerite, etc.
	Asphaltes		Asphalt(um)
	Pure or fairly pure		Asphaltes
	Calcareous	Patty acid pitches ("stearin pitch")	
From asphalts	Silicious		From Bones
	Earthy		From Fats
	Gilsonite		From Vegetable Oils
From vegetable growths	Glance pitch	Resin pitch	From Saps of Coniferae
	Manjak		From Wood and Roots of Coniferae
	Grahamite		From Hard Woods
	Wurtzilite (elaterite)		From Petroleum
Bituminous shiats	Alberite	Stearin pitch ("candle tar")	From Maltha
	Imposonite		From Peat
	Peat		From Lignite
	Lignite	Wool-fat pitch ("wool pitch")	From Bituminous Coal
Bituminous shales	Anthracite		From Bituminous Shales
From Bones		Palm-oil pitch	
From Fats		Cottonseed-oil pitch	
From Vegetable Oils		From Saps of Coniferae	
From Saps of Coniferae		From Wood and Roots of Coniferae	
From Wood and Roots of Coniferae		From Hard Woods (e. g., oak, maple, birch and beech)	
From Petroleum		Water-gas tar and water gas-tar pitch	
From Maltha		Sludge pitch	
From Ozokerite, etc.		Petroleum asphalt (petroleum pitch)	
From Peat		Blown (oxidized) petroleum asphalt	
From Lignite		Asphalt(um)	
From Bituminous Coal		Paraffin, etc.	
From Bituminous Shales		Peat tar and peat-tar pitch	
From Elaterite		Lignite tar (brown-coal tar) and lignite-tar pitch	
From Bituminous Shales		Coal tar and coal-tar pitch	
From Elaterite		Coke-oven tar and coke-oven-tar pitch	
From Bituminous Shales		Blast-furnace tar and blast-furnace-tar pitch	
From Elaterite		Generator-gas tar and generator-gas-tar pitch	
From Bituminous Shales		Elaterite pitch	
From Bituminous Shales		Shale oil and shale-oil pitch	

Resin (colophony)
 Certain of the copals (recent origin)
 Sandarac
 Shellac
 Anime
 Damar
 Elemi
 Mastic
 Amber
 Certain of copals

Bone-tar pitch
 Fatty-acid pitch
 Fatty-acid pitch
 Oxidized oils
 "stearin pitch"

Resin pitch
 Certain varieties of pine tar
 Pine-tar pitch

Water-gas-tar pitch
 Sludge pitch
 Petroleum asphalts
 Blown petroleum asphalts

Asphalt(um)
 Peat-tar pitch
 Lignite-tar pitch

Coal-tar pitch
 Coke-oven-tar pitch
 Blast-furnace-tar pitch
 Generator-gas-tar pitch

Elaterite pitch
 Shale-oil pitch

³ Obtained from distillation of bitumens: This includes petroleum pitch, either "straight" or "cut back."

⁴ Obtained from the "oxidation" of bitumens: This includes "blown" petroleum pitches.

⁵ Obtained from the "sulfurization" of bitumens: This includes the so-called "Dubb's asphalt," obtained by heating petroleum residues with sulfur.

⁶ Variable Origin: It may be of animal, vegetable or mineral origin and includes both natural and artificial products.

⁷ Hydrocarbon Complex: Often contains oxygen, nitrogen or sulfur derivatives of the hydrocarbons. This excludes vegetable resins, vegetable and animal waxes, etc.

⁸ Associated with a mineral matrix: This may be calcareous, siliceous, earthy, etc., which is usually present as an impurity.

⁹ Solutions in essential oils: The essential oils consisting of terpenes.

¹⁰ Variable Compositions: No exact chemical composition. Usually mixtures of closely related substances, composed of the elements carbon and hydrogen, together with varying amounts of oxygen, sulfur and nitrogen. May contain hydrocarbons, fats, fatty acids, resin acids, waxes, etc., etc., or mixtures of these.

¹¹ Insoluble in water: This excludes gum resins, carbohydrates, etc.

¹² Partly soluble in water: The carbohydrates ("gums") are the soluble constituents.

¹³ Soluble in carbon disulfide, benzol, etc.: This does not take into consideration the mineral constituents present and excludes the pyro bitumens.

¹⁴ Relatively insoluble in carbon disulfide, benzol, etc.: This likewise does not take into consideration the mineral constituents present and excludes the bitumens proper, tars, and most pitches.

¹⁵ Viscous: This excludes gaseous and solid bitumens.

¹⁶ Viscous to semi-solid: This is governed by the amount of essential oil present.

¹⁷ Viscous to solid: Some occur as sticky masses, others as hard and brittle solids at ordinary temperatures. Plasticity is an inherent or an acquired property. Some are plastic at ordinary temperatures, others become plastic, under the influence of heat or when combined with suitable fluxes. This excludes the gaseous and liquid bitumens, tars and oleo resins.

¹⁸ Viscous to solid Bitumens and Pyro Bitumens: This includes the hard and relatively insoluble wood-tar pitches, etc.

¹⁹ Semi-solid to solid: Usually contains small amounts of essential oils, which govern the consistency.

²⁰ Solid: This excludes gaseous, liquid and viscous substances.

²¹ Variable Hardness: This includes gaseous (in the case of bitumens), also liquid, viscous and solid substances.

²² Light Colored in Mass: This excludes the mineral resins.

²³ Dark Colored in Mass: Usually black. This excludes paraffin (ceresine), and vegetable resins.

²⁴ Variable Color in Mass: Color ranges from pure white (paraffin wax), to very dark, almost black (ozokerite and montan wax).

²⁵ Amorphous Structure: In distinction to crystalline.

²⁶ Conchoidal Fracture: But sometimes "hackly."

²⁷ Waxy Lustre: Mineral waxes have a waxy lustre, and are, therefore, included.

²⁸ Resinous Lustre: This together with the light color is characteristic of the true resins.

²⁹ Non-adherent to slightly adherent feel: In distinction to the unctuous feel of waxes.

³⁰ Uctuous Feel: This is characteristic of waxes.

³¹ Tarry Odor: Most tars have a characteristic odor, but some mineral tars (e. g., maltha, petroleum tars, etc.) are practically free from odor.

³² Extremely susceptible to changes in temperature: Meaning that they pass rapidly from the solid to the liquid state as the temperature is raised (i. e., have a high "susceptibility factor").

³³ Fusible: Soften on warming, melt without decomposition, decompose as the temperature is increased, and finally burn with a smoky flame, leaving a carbonaceous residue behind. This excludes the asphaltites, as these are difficultly fusible, and the pyro bitumens as these are infusible (but which, however, decompose and melt at higher temperatures).

³⁴ Difficultly Fusible: Intermediate between the natural asphalt and pyro bitumens.

³⁵ Infusible: This excludes the bitumens proper, vegetable resins, tars, pitches, etc.

The chart on page 14 shows the relation between bituminous substances, bitumens, pyro bitumens, maltha, asphaltum, asphaltite, tars and pitches; also between resinous substances, true resins, oleo resins, gum resins and mineral resins.

BOUND BROOK
NEW JERSEY

THE EFFECT OF EXPOSURE ON BITUMENS¹

By PRÉVOST HUBBARD AND C. S. REEVE

It is a well known fact that in all types of bitumens changes occur upon aging and exposure. These changes often result in noticeable variations in characteristics which are at least qualitatively apparent to the casual observer. They may be the result of purely physical phenomena or of chemical reactions which take place either between certain inherent constituents of the bitumens themselves or between the bitumens and some external agent. Thus loss of the lighter oils by volatilization may be considered a purely physical cause of change while molecular rearrangements, inter-reactions and the oxidation of certain constituents are examples of chemical changes.

The object of our investigation was to determine the nature of changes due to exposure which take place in various types of bitumens, particularly those used in the treatment and construction of roads and pavements. At the outset it was realized that to exactly duplicate service conditions in a laboratory test would be impracticable if not impossible but an attempt was made to approach these conditions as nearly as possible. Eight samples of bituminous road materials were selected for the following experiments as representing the principal types in common use. The results of the usual examination of these materials are given below. These and all other analyses reported in this paper were made according to methods which we have published² elsewhere and which, therefore, need not be described here.

The form of box in which the exposures were made is shown in Fig. 1. This box was made of $\frac{3}{4}$ inch wood, and its interior dimensions were $25 \times 14\frac{1}{2} \times$

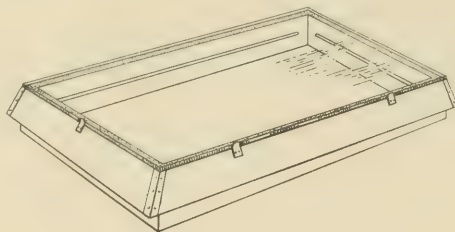


FIG. 1.—EXPOSURE BOX

2 inches. A felt rim surrounded the upper edge and upon this rested a $\frac{1}{4}$ inch plate-glass cover. To provide for some circulation of air, a $\frac{1}{4}$ inch slot was cut through each of the sides as shown in the sketch, and a thin board extended from the upper edge at an angle of about 45° to prevent dust and rain from entering through the slot.

At first strips of cheese-cloth were stretched between the bottom and the edge of the slanting side board, but when it was found that this did not insure perfect freedom from dust, cotton batting was loosely packed beneath the slanting board and against the

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² Bull. 38, Office of Public Roads, U. S. Department of Agriculture.

ventilating slot. This successfully excluded dust and permitted a fair circulation of air.

The samples were placed in Syracuse watch glasses, as shown in the illustration (Fig II). The depressions in these glasses are approximately 47 mm. in diameter, by 8 mm. deep, and they were filled to a uniform depth of 32 mm. with each of the materials to be exposed. The samples were melted and thoroughly stirred, and each set of specimens was made at one pouring, the depth of bitumen being obtained by means of a gauge immersed in it.

The several types of material selected and their characteristics are shown in the following tables:

TABLE I—OIL AND ASPHALT PRODUCTS

	Fluxed Bermudez asphalt	Gilsonite oil asphalt	Oil asphalt	Semi asphaltic petroleum residuum	California petroleum residuum
Specific gravity 25° C./25° C.	1.040	0.958	0.985	0.936	0.998
Consistency	51 ¹	243 ¹	228 ¹	31.2 ²	8' 8" ³
% Loss 163° C., 5 hours	..	1.71	0.43	3.75	0.49
Consistency of residue	..	184 ¹	137 ¹	fluid	12' 1" ³
Bitumen soluble in CS ₂	96.43	99.67	99.70	99.96	99.88
Organic matter insoluble	1.62	0.13	0.19	0.02	0.08
Inorganic matter insoluble	1.95	0.20	0.11	0.02	0.04
% Bitumen insoluble in 86° B. naphtha	25.16	22.16	20.27	1.93	6.57
% Fixed carbon	12.10	8.87	11.98	4.07	5.67

¹ Penetration 100 g., 5 sec., 25° C.

³ Float test 32° C.

² Specific viscosity (Engler) 50° C.

TABLE II—TAR PRODUCTS

	Refined coal tar	Refined water-gas tar	Refined mixed coal and water-gas tar
Specific gravity 25° C./25° C.	1.227	1.174	1.240
Float test 50° C.	1' 54"	2' 38"	5' 0"
% Free carbon	17.31	0.60	15.80
Distillation (by weight) ¹
Light oils to 110° C.	0.1	0.44	..
2nd Light oils 110° C.-170° C.	0.62	0.43	..
Dead oils 170° C.-270° C.	21.53	17.86	..
Pitch residue	77.3	81.4	..

¹ 250 cc. sample, 750 cc. glass retort, bottom of thermometer bulb level with bottom juncture of stem and body of retort. Method since discontinued.

² 9/10 solid.

³ Slightly cloudy.

³ 1/4 solid.

⁴ Not sufficient sample for distillation.

⁴ Clear.

Six rows, each of which contained one set of the samples, were placed lengthwise of the box. The box was then set with its length east and west outside a window having an open southern exposure.

of comparison with the original analyses. The watch glasses and their contents were first weighed for the purpose of determining any change in weight since placing them in the box. The changes in weight were found to be so slight at this time that no other tests were made. At the end of two months another set of samples was removed and weighed. Owing to cold winter weather the changes in weight were still very small but in general somewhat greater than at the end of one month. At this time, after melting and thorough stirring, portions of each sample were, if sufficiently hard, subjected to the penetration test at 25° C. If too soft for the penetration test a float test was made at 40° C.

The relative degree of hardening due to exposure for this period of time was thus determined. Solubility determinations were then made on another portion of each sample. For the petroleum and asphalt products, 86° B. paraffin naphtha was used as a solvent while c. p. carbon disulfide was used for the tar products. The solutions were filtered through a Gooch crucible fitted with an asbestos pad and the insoluble organic matter determined by weighing the residue before and after ignition. The organic matter insoluble in naphtha was determined on the basis of total bitumen.

All of these tests were repeated at the end of four, six, eight and twelve months' exposure. The results thus obtained are given in the following tables. At the end of each period the general appearance of the samples was noted as described later. At the end of the twelve-month period, a set of samples were photographed for the purpose of showing the very marked differences in the surface appearance of the various bitumens due to exposure. In order to assure ourselves that accumulations of dust could not be held responsible for gain in insoluble organic matter, a large number of determinations of the organic material insoluble in carbon disulfide was made at different periods on the oil and asphalt products. In no case, however, was any appreciable gain to be detected as compared with the original determinations.

In reviewing Table III, it will be noted that the tests were begun during midwinter when changes due to loss by volatilization should be at a minimum. At the end of one month it was found that only the tars and the fluid semi-asphaltic petroleum residuum

TABLE III—CHANGES IN WEIGHT AND CONSISTENCY

	Dec. 9		Jan. 9		Feb. 9		April 9		June 9		Aug. 9		Dec. 9	
	Original		1 month		2 months		4 months		6 months		8 months		12 months	
	Pen	Float	% Wt.	Pen	% Wt.	Pen	Float	% Wt.	Pen	Float	% Wt.	Pen	% Wt.	Pen
Fluxed Bermudez asphalt	51	..	+0.05	..	+0.08	43	..	+0.14	36	..	-0.34	26	..	-0.59 15
Gilsonite-oil asphalt	243	..	+0.06	..	+0.09	219	..	+0.47	203	..	+0.09	139	..	+0.66 119
Oil asphalt	228	..	+0.04	..	+0.10	184	..	+0.35	164	..	+0.81	82	..	+1.88 98
Semi-asphaltic petroleum residuum	fluid	..	-0.30	fluid	-0.26	fluid
California petroleum residuum	3' 43"	..	+0.08	..	+0.13	..	4' 30"	+0.98	..	5' 8"	+1.48	..	15' 5"	+2.25 61
Refined coal tar	3' 46"	..	-0.25	..	-0.25	..	4' 22"	-3.04	..	14' 12"	-8.52	16	..	-9.58 9
Refined water-gas tar	5' 14"	..	-0.11	..	-0.07	..	6' 58"	-2.59	..	18' 48"	-9.54	9	..	-11.06 8
Refined mixed tar	128	..	-0.05	..	-0.02	124	..	-1.05	89	..	-5.05	19	..	-6.00 12

After exposing these samples for a period of one month an entire set was removed from the exposure box and subjected to certain tests for the purpose

had suffered any loss by volatilization and as would be expected these losses were very small. All of the other materials showed a slight gain in weight. At

the end of two months approximately the same situation prevailed although the samples which had previously gained in weight showed a slight additional gain. All of the materials had become somewhat harder with the exception of the refined mixed tar and the semi-asphaltic petroleum residuum which latter was too fluid to permit of a penetration or float determination being made. In the early part of April at the end of four months, the loss in weight

though in tars such loss is probably responsible to a considerable degree for the hardening of these products. The hardening of petroleum and asphalt products is undoubtedly due to oxidation which proceeds slowly at comparatively low temperatures but increases at higher temperatures. It seems probable that oxidation also plays a part in the hardening of tars although the preceding data does not absolutely prove this fact.

TABLE IV—PERCENTAGE GAIN IN INSOLUBLE ORGANIC MATTER

	2 months			4 months			6 months			8 months			12 months		
	Insoluble in 86° B. Petroleum Naphtha														
	Original	Actual	Calculated	Actual	Calculated	Actual	Calculated	Actual	Calculated	Actual	Calculated	Actual	Calculated		
Fluxed Bermudez asphalt.....	25.16	0.65	—0.02	1.34	—0.05	4.50	0.09	7.24	0.15	9.42	0.35				
Gilsonite—oil asphalt.....	22.42	0.53	—0.02	1.18	—0.09	2.68	—0.02	3.57	—0.13	4.07	0.19				
Oil asphalt.....	20.27	0.30	—0.02	0.54	—0.07	4.33	—0.16	6.13	—0.38	6.10	—0.19				
Semi-asphaltic petroleum residuum.....	1.93	1.42	0.01	3.06	...	6.24		
California petroleum residuum.....	6.57	0.88	—0.01	2.53	—0.07	9.78	—0.10	12.35	—0.15	12.96	—0.12				
	Insoluble in Carbon Disulfide														
Refined coal tar.....	17.31	0.82	0.04	1.93	0.54	4.64	1.61	6.34	1.83	6.42	1.87				
Refined water-gas tar.....	0.60	0.27	0.00	0.75	0.02	2.61	0.06	3.80	0.07	4.08	0.08				
Refined mixed tar.....	15.80	0.67	0.00	1.08	0.17	3.70	0.84	5.53	1.01	5.26	1.01				

of the tar samples was quite appreciable running from about 1 to 3 per cent. The petroleum and asphalt products, however, showed a continued increase in weight. At this time it was found that all of the semi-asphaltic petroleum samples had crept over the edge of the watch glasses so that accurate weight determinations could not be made upon them from then on. All of the other materials showed a continued increase in hardness which increase persisted throughout the entire test.

Just before the withdrawal of the samples for the tests at this period, the weather suddenly became warm for several days, and there was an immediate formation of an oily layer upon the lower side of the glass cover. This rapidly increased and after a short time became a thin, hard varnish-like crust which adhered firmly to the glass. Upon attempting to remove it, it was found to be very sparingly soluble in either carbon disulfide or benzol. It was found to be partially soluble in 95 per cent. alcohol with the production of an amber colored solution, and a brownish, insoluble powder. From contemporaneous investigations we have found this to be produced principally as an alteration production of the volatile portion of the tars.

At the end of six months the fluxed Bermudez asphalt was found to have slightly decreased in weight. The petroleum products, however, showed a notable increase in weight, particularly the California residuum. The same was apparent at the end of 8 months at which time, due to warm weather, the loss in weight of the tar samples had almost reached a maximum for the entire 12 months' test. At the end of one year only the California residuum and oil asphalt showed an increase in weight. All of the products were sufficiently hard to permit of penetration determinations being made.

It is apparent from these results that the hardening of all bitumens upon exposure is not due to loss by volatilization of the lighter constituents, alone, al-

In Table IV, the percentage increase in insoluble organic matter of the eight materials at different periods of exposure is given together with the calculated increase or decrease based upon their loss or gain in weight at these periods. As previously stated, 86° B. paraffin naphtha was used as a solvent for the oil and asphalt products while c. p. carbon disulfide was employed for the tar products. This table need not be discussed in detail as practically all of the results show that exposure causes an increase in insoluble organic material which is considerably in excess of the increases calculated from their loss by volatilization. As compared with Table III it is apparent that this increase in insoluble material accompanies the increase in hardness and from what is known of the behavior of oil and asphalt products, upon being blown it would seem reasonable to suppose that such insoluble materials are the direct products of oxidation. Such products may actually contain oxygen or they may be the result of nucleus condensation brought about by the reaction of oxygen with two or more hydrocarbons originally present in the bitumens.

The increase in material insoluble in carbon disulfide for the tar samples may also have been caused by oxidation or molecular rearrangements and inter-reactions between certain constituents of the tar. That the latter type of reaction probably occurs to some extent has been shown by us in a recent paper.¹ It is believed that these results clearly demonstrate that so called "free carbon" is actually formed in tars upon exposure.

While the surface of all of the materials was smooth and glossy when first placed in the watch glasses considerable differences in their surface appearance and condition were apparent at different periods of exposure. Fig. II shows a photograph of the materials at the end of twelve months. At this time the observations given below Fig. II were made.

¹ Proc. Am. Soc. for Testing Materials, 11, 666 (1911).

In conclusion it should be stated that while the above results show interesting differences in the effect

in tending to change or modify the results obtained in the above described research.

INSTITUTE OF INDUSTRIAL RESEARCH
WASHINGTON, D. C.

EXAMPLES OF THE EFFICIENCY OF CALCIUM HYPOCHLORITE IN TREATING TURBID WATERS¹

By EDWARD BARTOW

We have recently had the privilege of noting the action of calcium hypochlorite in the purification of turbid waters in some of the plants in the North Central United States. Results from two of the plants illustrate in different ways the efficiency of the chemical. In one case the chemical was added at the end of a long sedimentation period, during which some reduction had taken place. The chemical reduced the number of bacteria very materially, and filtration was able to effect a still greater reduction. In the other case, owing to failure to receive a shipment of the chemical, none could be used for six days. There was at once a decided increase in the number of bacteria, followed by a decrease when the chemical was again applied even though the water, as shown by the turbidity, was the worst for years.

The results obtained in the first case are shown in Table I. The colony counts were obtained on gelatine at 20° C. The water treated was from the Mississippi River.

The number of colonies in the raw water is shown in the first column. The number of colonies in the effluent from a settling basin of twenty-four hours' capacity is shown in the second column. As a rule, the number was reduced. The average reduction was 65 per cent. The number of colonies in the water after treatment with calcium hypochlorite and approximately one and one-half hours additional sedimentation is shown in the third column. The number of colonies was further reduced 97.6 per cent. or 99.1 per cent. from the number in the raw water. The number of colonies obtained from the water after filtration is shown in the fourth column. There was a further reduction of 82 per cent. or a total bacterial removal of 99.8 per cent.

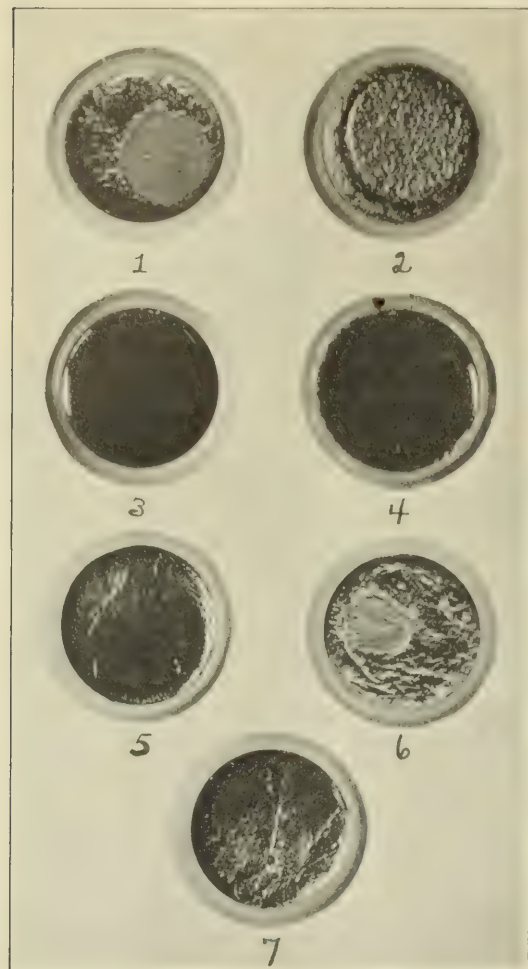


FIG. II.—BITUMENS AFTER 12 MONTHS' EXPOSURE

1. Flaxed Bermudez Asphalt: Portion of surface glossy and dark brown, showing an enclosed patch of about 1 inch diameter, dull and light brown.
2. Gilsonite Oil Asphalt: Surface bright but rough and granular.
3. Oil Asphalt: Smooth, bright, glossy surface.
4. California Petroleum Residuum: Smooth surface, glossy and sticky.
5. Refined Coal Tar: Surface drawn and cracked in places. Surface black; streak brown.
6. Refined Water Gas Tar: Surface wrinkled and showing large brown patch of about 1/2 inch diameter. General crystalline appearance.
7. Refined Mixed Tar: Surface drawn and cracked. Friable black film; streak brown.

of exposure upon characteristic types of bituminous materials, they should not, for practical purposes, be too positively or rigidly interpreted. When these materials are exposed to an actual service test in connection with the particular purpose for which they are to be used, other factors undoubtedly play a part

TABLE I.—COLONIES GROWING ON GELATINE AT 20° C. IN 48 HOURS

Date	Raw	After sedimentation	After hypochlorite	Filter effluent
Oct. 17, 1910.....	28,000	9,700	95	75
Nov. 23, 1910.....	2,300	2,200	47	17
Dec. 18, 1910.....	5,600	1,200	70	31
Feb. 6, 1911.....	46,500	11,000	690	44
May 4, 1911.....	26,500	3,300	370	40
Aug. 15, 1911.....	13,000	280	50	8
Sept. 12, 1911.....	19,000	5,000	37	17
Oct. 18, 1911.....	5,400	2,800	170	72
Jan. 25, 1912.....	500	17,000	45	12
Mar. 29, 1912.....	67,000	22,000	260	10
Average, 21,380		7,448	183	33

Tests for gas forming bacteria were made on the same samples of water and the results correspond very well with the reduction in the number of bacteria.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

The results are shown in Table II. The treatment with calcium hypochlorite has entirely eliminated the gas formers from the 0.1 cc. samples, from 86 per cent. of the 1 cc. samples and from 50 per cent. of the 10 cc. samples. The filtration has improved conditions by increasing the removal to 91 per cent. of the 1 cc. samples and to 73 per cent. of the 10 cc. samples. From these observations we may conclude that the calcium hypochlorite acts most efficiently in the removal of free bacteria, that the filters still further reduce the numbers by removing aggregates of bacteria which are surrounded by or enclosed in sediment.

TABLE II

FORMATION OF GAS IN DEXTROSE BROTH AT 37½° C.

Raw.....	10 cc.	11+	1—
	1 cc.	20+	3—
	0.1 cc.	18+	4—
After sedimentation.....	10 cc.	10+	0—
	1 cc.	18+	2—
	0.1 cc.	14+	7—
After hypochlorite.....	10 cc.	6+	6—
	1 cc.	3+	18—
	0.1 cc.	0+	22—
Filter effluent.....	10 cc.	3+	8—
	1 cc.	2+	20—
	0.1 cc.	0+	22—

In the second example of the efficiency of calcium hypochlorite none of the chemical was used for six days, owing to the failure to receive a shipment. In the treatment plant lime and iron sulfate were used

is added not more than five minutes before the water reaches the filters.

The water during the three six-day periods, before, during and after the failure to receive the calcium hypochlorite, was especially bad (see Table III) as was shown by the high turbidity and the large number of colonies that developed from the raw water during forty-eight hours on gelatine at 20° C. After the first two days of the first period the number of bacteria in the raw water were never lower than 20,000. Only once was the turbidity below 200, reaching a maximum of 4,000 during the latter part of the period. As shown in Table III, the bacterial removal during the six days preceding the period without calcium hypochlorite was 99.9 per cent. and gas formers were entirely absent in the general effluent from the filters. During the period without calcium hypochlorite the bacterial removal was only 93.9 per cent. and gas formers were present in the effluent with the exception of the test made on the first day without calcium hypochlorite. During the six days following the period without calcium hypochlorite the bacterial removal was again 99.9 per cent. and gas formers were absent in all of the samples tested.

These results show very decidedly the advisability of using calcium hypochlorite under conditions similar to those existing in the plants in question.

UNIVERSITY OF ILLINOIS
URBANA

TABLE III

OPERATING RESULTS WITH AND WITHOUT CALCIUM HYPOCHLORITE¹

Date, 1912	Turbidity	Bacteria		Gas formation		Parts per million chlorine
		Raw	Filter effluent	Raw	Filter effluent	
Mar. 13.....	25	1600	3	+	—	0.51
Mar. 14.....	25	3900	10	+	—	0.51
Mar. 15.....	210	90000	200	+	—	0.55
Mar. 16.....	230	400000	275	+	—	0.45
Mar. 17.....	500	27000	50	+	—	0.53
Mar. 18.....	800	125000	20	+	—	0.48
Average six days preceding period without hypochlorite.....	298	107917	93	100%+	None+	0.50
Mar. 20.....	300	112000	8400	+	—	0.00
Mar. 21.....	400	110000	7500	+	—	0.00
Mar. 22.....	150	60000	2000	+	—	0.00
Mar. 23.....	825	44000	1700	+	—	0.00
Mar. 24.....	400	56000	2000	+	—	0.00
Mar. 25.....	320	20000	3000	+	—	0.00
Average during period without hypochlorite.....	399	67000	4100	All+	83.3%+	None
Mar. 26.....	200	20000	30	+	—	0.48
Mar. 27.....	220	160000	120	+	—	0.57
Mar. 28.....	450	75000	80	+	—	0.55
Mar. 29.....	4000	300000	120	+	—	0.60
Mar. 30.....	4000	300000	550	+	—	0.47
Mar. 31.....	350	250000	200	+	—	0.47
Average six days following period without hypochlorite.....	1537	184170	183	All+	None+	0.52

¹ Analyses by H. M. Ely, Danville, Illinois.

as coagulants. The amounts used were varied in such a way as to furnish a clear water. The calcium hypochlorite was used as an adjunct. There is approximately one hour's sedimentation after the lime and iron sulfate are added. The calcium hypochlorite

COMPOSITION OF THE SALINES OF THE UNITED STATES¹

III. Brines from the Ocean and Salt Lakes

By J. W. TURRENTINE, with analyses by W. H. ROSS, A. R. MERZ AND R. F. GARDNER

Received October 9, 1912

In the search for deposits of potassium salts in the United States two sorts of deposits have been considered, namely, continental and marine. The former, continental, are those which have resulted from the desiccation of inland seas or lakes; while the latter, marine, are the product of the evaporation of arms of the ocean which have become isolated from the main body of the ocean through the formation of bar reefs. The latter method would be analogous to that generally proposed to account for the formation of the Stassfurt deposits.

Among the saline deposits in the United States, theoretically, are deposits of both kinds. These have been (or are being) subjected to scrutiny to discover if there may be potassium salts therein, as well as sodium. The search for continental deposits has confined itself to those regions which it is known were once covered by inland seas. This statement connotes the fact that such lakes were of sufficiently recent occurrence for their marks to have remained extant on the face of the country where they existed. It is not sufficient that those areas were submerged by lakes, but for deposits of salt to have formed, it is necessary that the lakes shall have disappeared through desiccation rather than through drainage.

Continental deposits have been sought in the undrained basins of the western part of the United

¹ Published by permission of the Secretary of Agriculture.

States. As the basins are unfilled by sedimentary or detrital material it was hoped that the saline residues would be found on the floor of the basins. Such has been the case in some instances, while in others there are indications that sufficient detrital matter has been carried into the lowest depressions of the basins to cover any saline matter once deposited there.

The undrained basins of the west may be classified as follows: (I) The Lahontan Basin; (II) the Lake Bonneville Basin; (III) the group of small basins found in southern and central California and southern Nevada; and (IV) other basins of slight importance, such as the Salton Basin, formerly of great interest, but now resubmerged; the lake basins of northeastern California and southeastern Oregon and arid basins of New Mexico and small basins bordering the arid area.

I. THE LAHONTAN BASIN

The core of the basin in the northwestern and central part of Nevada, during the quaternary period of greatest lake expansion, was a single great lake. Its history has been studied by Russell,¹ who gave it the name Lake Lahontan. The basin is nearly a unit, the divides now evident being low or discontinuous. The old lake at present is represented by a few remnants, such as the Pyramid, Winnemucca and Walker Lakes and a number of sinks, playas and saline marshes. The salts now present on its surface, in the form of crusts or brines, are certainly far less than the salts which one reasonably can assume to have been present in the larger lake. Russell accordingly has assumed that the saline material has been buried by alluvial coverings, and subsequent investigation has tended to uphold this conclusion. It is reasonably certain that the original saline constituents of the Lake Lahontan water underlie the floor of the parent basin, either as crystalline deposits or as salt-impregnated strata of alluvial material.

The rocks of the basin and its drainage area are largely igneous, though for the most part non-potassic. Consequently it is to be concluded that the salts in the early lake were largely sodium salts and alkaline in character. From an examination of surface conditions, it is impossible to say whether, in the deposition of these salts, the potassium was crystallized at all or, if so, whether in segregated strata or as a crystalline mixture; or whether the mother liquor from the sodium salts deposition, containing the potassium salts, was or was not disseminated through the saline and alluvial strata. These questions can be settled only by boring, a work which the U. S. Geological Survey is now undertaking. Already a boring to the depth of several hundred feet has been sunk in the Humboldt Basin, a depression of the Lahontan, where the surface conditions indicate that the bottom of the basin may be reached. So far, only alluvial matter has been encountered, and the water obtained from the boring, instead of being a brine, is surprisingly fresh.

II. BONNEVILLE BASIN

In northwestern Utah and extending across the

state borders into eastern Nevada is a somewhat larger basin recorded by Gilbert² as Lake Bonneville. This basin is also a topographic unit and was once occupied by a great quaternary lake. The last remnant of this lake is found in the present Great Salt Lake of Utah. The Bonneville Basin differs from the Lahontan in that it is set in Paleozoic sediments instead of rocks of igneous origin. It is to be expected, therefore, that its salines are largely neutral salts, rather than alkaline, consisting mostly of the chlorides and sulfates of sodium and magnesium. That such is actually the case is seen from the analyses of the water of Great Salt Lake.³

It is to be expected that potassium salts would have been present in Lake Bonneville only in small amounts, and such seems to be the case from the analysis of the Great Salt Lake water. It is possible that, at some previous time, the lake may have gone completely to dryness, when the saline accumulation of the preceding age was deposited, and that the salts of the present lake represent the accumulation of more recent age. There is no evidence at hand, however, by which to substantiate such a supposition.

Desiccation has taken place in the Great Salt Lake to the point of saturation with respect to sodium sulfate and of high concentration in sodium chloride. Crystallization is now taking place in the lake to the extent, at least, that sodium sulfate precipitates during cold weather, forming a crystalline crust on the surface. The crystals doubtless fall to the bottom of the lake, though it has not been established that there is an accumulation of saline material on the bottom.

Neither the probable geological history of the Bonneville Basin nor the character of the rocks in which it lies offers any indication of the presence of segregations of potash, and a negative conclusion may be considered warrantable.

III. THE GROUP OF SMALL BASINS FOUND IN CENTRAL AND SOUTHERN CALIFORNIA AND SOUTHERN NEVADA

The region south and southwest of the Lahontan Basin is similarly lacking in seaward drainage. This area likewise was occupied by lakes during an earlier period. The topography of the country is such that it is divided by high and continuous mountains into a number of small basins, each with its individual characteristics. In this area are included the Mojave Desert and Searles, Saline, Amargosa and Death Valleys. The rimmocks of these basins are varied and have been but little studied. It is known, however, that surrounding them lie rocks of both igneous and sedimentary origin. The basement granites of the Sierra Nevada are exposed in places in the western part of the area, especially toward the south.

Searles Lake.—Of particular interest among the basins of this group is the Searles Marsh, or Lake, in San Bernardino County, California, which has been found in the last stages of desiccation. At present the lake, or dried-up remnant of a lake, covers an area of 11 square miles and is of unknown depth. It is covered by a crust of saline material, beneath which

¹ Monograph XI, U. S. Geological Survey.

² Monograph I, U. S. Geological Survey.

³ "Data of Geochemistry," Clarke, *U. S. Geological Surv. Bulletin*, 491.

lies a mixture of saline and clayey material. The saline crust has a thickness of 75 to 100 feet and is composed principally of sodium chloride, sulfate, carbonate and borate. Considerable segregation has taken place in the crust, though the stratification is not at all well defined. And there is no strict demarcation between the saline and clayey strata, but rather a gradual transition from the one to the other.

Various crystalline, saline minerals are found intermixed with the loosely-defined strata. Among these are halite (NaCl), thenardite (Na_2SO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$), borax, hanksite ($\text{Na}_{22}\text{K}(\text{SO}_4)_9(\text{CO}_3)_2\text{Cl}$), etc.¹ Both the saline and clayey strata are impregnated with brine.

The analyses of the Searles brines, reported below in Table I, were made by Mr. A. R. Merz, of the Co-operative Laboratory, Mackay School of Mines, Reno, Nevada, and were duplicated by Mr. J. G. Smith, of the Bureau of Soils.

TABLE I—ANALYSES OF BRINES FROM SEARLES LAKE. POTASSIUM OXIDE RECORDED AS PER CENT. OF TOTAL SOLIDS

Sample number.....	198	199	200	201	202	203
Total solids, grams per 100 cc.....	44.29	44.69	43.66	42.86	43.96	43.45
Potassium oxide.....	7.63	6.23	6.89	6.06	7.27	6.57

The system which is represented by the Searles Lake brines—one containing chlorides, sulfates, carbonates and borates of sodium and potassium—is extremely complex. It cannot be accurately foretold, therefore, what the conditions controlling the separation of potassium salts therefrom will prove to be, or with what ease or difficulty the separation may be made. Since the carbonate and borate are among the more valuable of the various possible products of the lake, the potassium salts may be produced as a by-product. A study of the system, sodium chloride, sodium sulfate, sodium carbonate, sodium borate, potassium chloride, potassium sulfate, potassium carbonate, potassium borate, and water, or, in short, the system represented by the water of alkaline lakes and typified by the brine of Searles Lake, is being studied in the laboratories of the Bureau of Soils, with a view to the separation of potassium salts from such brines.²

The following complete analysis of the brine from the Searles Marsh is by Dr. W. H. Ross, of the Bureau of Soils.

TABLE II—ANALYSIS OF BRINE FROM SEARLES LAKE. EXPRESSED IN PERCENTAGES OF THE ANHYDROUS SOLIDS

Na	33.57	Ca	none	SiO ₂	0.023	CO ₂	6.70
K	6.06	Mg	trace	Cl	37.02	PO ₄	0.30
Li	0.01	Mn	none	Br	0.094	NO ₃	none
Rb	none	Cu	none	I	0.004	As ₂ O ₃	0.083
Ba	none	Al ₂ O ₃	0.012	SO ₄	12.96	P ₂ O ₇	3.00
NH ₄	none	Fe ₂ O ₃	0.003				

¹ This statement is made on the basis of recent observations. The Searles Marsh has been described by Wm. Ireland, Mineralogist, in the 10th Ann. Rpt. State Mineralogist, Cal. State Mining Bureau, pp. 334-9, 1890.

² The chemico-engineering problems involved in the extraction of potassium salts from the Searles brine have been investigated during the past summer by Mr. John W. Hornsey, Consulting Engineer, 49 Wall Street, New York City. As a result of the successful outcome of these investigations, we are informed by Mr. Hornsey, under date of December 27th, that the operating company has begun the erection of the first of four units of an extracting plant with a capacity of about 125 tons of potassium chloride per day. It is intended to increase this to a production of about 500 tons per day. In addition to potassium chloride the plant will produce soda ash and borax, with the probability of adding other products later.

The sample was collected by Mr. E. E. Free, of the same Bureau, from a well on the marsh designated as A7.

Additional results, in the following table, are expressed in percentages of the original brine, by weight. The weight of the total solids was taken after drying at 110° C., and includes some water of hydration, and organic matter. This is expressed by the value recorded as loss on ignition.

TABLE III

Total solids, at 110° C.....	30.34	Sodium carbonate in solution 3.04	
Loss on ignition.....	0.69	Sodium bicarbonate in soln. 0.75	
Anhydrous solid.....	29.65	Potash, K ₂ O.....	2.17

Railroad Valley.—It has been long known that the brines of Railroad Valley, Nevada, contain a remarkably high percentage of potassium salts. The recent analyses of various samples of these brines, performed by A. R. Merz, are given in the subjoined table.

The potassic brines of this valley, however, are found impregnating the detrital material on the floor of the depression and, as are the brines of many such basins, are confined to the upper portion of this material. The composition of these brines in the various parts of the flat are extremely variable, not only in concentration but in the relative proportion of the various salts.

The exploration of the valley is being continued by the Railroad Valley Saline Company. This company has sunk a well which at present has reached a depth of 1200 feet and has not yet reached the bottom of the original lake which submerged this valley. Large volumes of fresh water, artesian in character of flow, are now obtainable from this boring.¹ Following is given the log of the well as recorded in a report on "Potash," by E. E. Free and published by the exploitation company.

LOG OF RAILROAD VALLEY HOLE

Feet		
1-32	Sand with occasional clay layers	
32-103	Quicksand	
103-132	Alternations of quicksand and clay	Artesian water, especially at 128 ft.
132-136	White clay with small seams of fine gravel or coarse quicksand	
136-178	Heavy clay	
178-214	Quicksand	Artesian water
214-285	Alternations of clay and sand, layers 1 ft' to 10 ft. thick	Artesian water in most of the sands, especially at 220 and 250 ft.
285-305	Sand, coarser in upper part. Pebbles 3-4 in. in diameter at 285 ft.	Artesian water
305-336	Tough clay	
336-340	Quicksand with some clay and some small gravel	Artesian water
340-365	Clay, with occasional streaks of quicksand	
365-375	Quicksand with very small streaks of clay	Artesian water
375-390	Tough, gray clay	
390-391	Quicksand	Small artesian flow
391-418	Tough, gray clay	
418-419	Quicksand	Small artesian flow
419-429	Brown clay	
429-430	Quicksand	Small artesian flow
430-460	Clay, gray in lower part, changing to brown in upper	
460-461	Quicksand	Artesian water
462-470	Blue-green clay, with a white layer on top	

¹ We are advised by Mr. Hoyt S. Gale, of the U. S. Geological Survey, that similar fresh water is being met at about the same depth in the boring he is supervising near Fallon, Nevada, in the Lahontan Basin. It may, perhaps, be regarded as a sign of great promise indicating that there is no great dissemination of salines in the detrital fill of these basins, and *per contra*, that there are segregated salt layers somewhere below the surface, though at what depth cannot be predicted as yet.

LOG OF RAILROAD VALLEY HOLE (Continued)

TABLE IV—ANALYSES OF BRINES AND SALINE CRUSTS FROM RAILROAD VALLEY, NEVADA. A. R. MERZ, ANALYST. TOTAL SOLIDS AS GRAMS PER 100 CC. POTASSIUM OXIDE AS PERCENTAGE OF TOTAL SOLIDS

Feet				Sample no.	Total solids	Per- centage K ₂ O	Sample no.	Total solids	Per- centage K ₂ O	Sample no.	Total solids	Per- centage K ₂ O
470-471	Quicksand	Artesian water		1	33.86	9.06	91	70.97	6.97	127	76.40	3.68
471-478	Lead colored clay			2	44.08	9.87	92	74.72	8.46	128	62.08	6.65
478-479	Very fine sand			3	55.20	12.19	93	56.37	7.54	129	55.22	2.73
479-500	White and blue green clays			4	49.10	10.02	94	16.68	3.98	130	20.87	8.54
500-504	Blue green clay with some coarse sand			5	58.32	7.18	95	53.00	7.39	131	83.40	4.53
504-519	White and blue-green clays	Artesian flow smell- ing of sulfuretted hydrogen		6	48.32	11.03	96	71.64	9.20	132	40.42	2.06
519-520	Quicksand			7	42.62	8.46	97	69.12	7.72	133	12.63	6.14
				26	2.07	5.25	98	55.16	9.22	134	13.04	6.23
				28	13.16	4.25	99	64.96	8.52	135	68.64	3.39
				30	6.22	6.52	100	66.62	5.76	137	14.18	1.81
29-533	Gray clay	Strong artesian flow		43	4.55	5.29	101	34.48	2.22	138	0.97	1.16
533-534	Very fine quicksand			45	27.36	5.03	102	55.18	8.96	139	47.18	1.30
534-539	Blue-green clay			48	33.98	3.10	103	43.24	3.90	143	15.74	5.94
539-541	Quicksand with some light colored clay and some coarse gravel			54	25.24	0.89	104	53.96	3.78	144	82.46	2.66
541-560	Yellowish, white and blue green clays			55	22.74	3.28	105	72.64	6.38	145	41.34	2.83
560-561	Quicksand	Artesian water		56	53.80	1.22	106	46.38	6.73	146	72.06	2.26
561-586	Blue-green and white clays			57	7.58	1.65	107	76.38	5.00	148	58.22	9.26
586-587	Quicksand	Small artesian flow		58	33.00	5.87	108	60.02	3.41	149	44.22	6.58
587-596	Clay			59	27.56	4.10	109	58.72	2.38	152	29.80	4.83
596-609	Alternations of sand and clay, the propor- tion of sand increasing downward	Small artesian flow, at 605 ft.		62	24.48	4.68	110	28.54	3.90	153	11.62	11.92
609-637	Clay, whiter in upper part			64	27.56	1.05	111	59.62	6.11	154	12.09	11.78
637-638	Quicksand			66	12.10	1.65	112	59.16	5.45	155	69.00	10.17
638-676	Tough clay, white and greenish in color			71	59.92	4.35	113	56.48	6.20	156	7.86	11.46
676-677	Quicksand			76	4.55	8.53	114	72.22	4.23	158	12.82	5.03
677-680	Alternations of clay and sand	Small artesian flow		80	58.22	6.85	115	41.24	1.53	159	67.92	3.79
680-691	White clay			81	56.63	2.98	116	10.56	6.02	162	48.92	1.48
691-700	Alternations of clay and sand			82	55.72	3.67	120	5.36	6.16	163	13.99	5.49
700-719	Clay, brownish on top			84	14.09	4.06	122	79.56	12.10	164	13.97	5.82
719-720	Sand			87	30.46	4.53	124	68.74	1.90	165	64.62	3.26
720-738	Brownish clay	Very small artesian flow		88	24.03	2.33	125	45.42	2.94	166	76.58	3.42
738-746	Clay and quicksand mixed. Some coarse gravel			89	25.58	5.71	126	56.90	5.04	168	41.10	1.53
746-759	Tough, brownish clay			90	49.48	7.91						
759-771	Sand alternating with very tough, brown- ish clay	Very small artesian flow in the sands										
771-785	Tough, brownish clay											
785-786	Quicksand	Artesian flow										
786-790	Clay											
790-791	Sandy streak in clay	Small artesian flow										
791-798	Brownish clay											
798-805	Alternations of clay and sand	Artesian water		306			Surface pond about middle of valley.....		36.51		3.42	
805-816	Clay, hard and brown in lower part			307			Shallow hole dug about 1/4 mile north of sink		20.36		1.08	
816-822	Quicksand and gravel			326			Water standing in slough about middle of valley.....		10.42		1.50	
822-824	Hard white clay			327			Water from ten-foot hole about middle of valley.....		36.81		3.31	
824-846	Clay and sand alternating every 2 to 6 in. Proportion of clay increases with depth	Strong artesian flow in all sand strata		331			Water from six-foot hole dug near Geol. Sur. bench mark in middle of valley. About 1 mile east of No. 327.....		33.80		0.96	
846-850	Brownish clay			338			Water from three-foot hole dug in north flat. (Cf. Table VI).....		33.28		3.08	
850-855	Sand and gravel			339			Water from three-foot hole dug near west side of valley west of Furnace Creek Ranch....		2.77		1.75	
855-865	Rapid alternations of clay and sand			341			Water from four-foot hole dug about middle of valley due west of Furnace Creek Ranch		15.12		2.38	
865-876	Gray clay			342			Water from three-foot hole dug near east side of valley, due west of Furnace Creek Ranch		34.18		2.98	
908-924	Sand and gravel	Strong artesian flow		343			Water from slough at old bridge, west of Furnace Creek Ranch.....		32.05		2.25	
924-934	Light and gray clay											
934-941	Fine sand											
941-945	Gray clay											
945-947	Sand											
947-967	Clay, yellow on top, gray below	Small artesian flow										
967-968	Sand and gravel											
968-1088	Hard, dry clay											
1088-1089	Dry sand											
1089-1175	Hard, dry clay											

Death Valley.—In Table V are given the analyses of a number of brines from Death Valley.

TABLE V—ANALYSES OF BRINES FROM DEATH VALLEY. A. R. MERZ, ANALYST. TOTAL SOLIDS RECORDED AS GRAMS PER 100 CC. POTASH AS PER CENT. OF TOTAL SOLIDS

Sample number	Location	Total solids	K ₂ O per cent.
306	Surface pond about middle of valley.....	36.51	3.42
307	Shallow hole dug about 1/4 mile north of sink	20.36	1.08
326	Water standing in slough about middle of valley.....	10.42	1.50
327	Water from ten-foot hole about middle of valley.....	36.81	3.31
331	Water from six-foot hole dug near Geol. Sur. bench mark in middle of valley. About 1 mile east of No. 327.....	33.80	0.96
338	Water from three-foot hole dug in north flat. (Cf. Table VI).....	33.28	3.08
339	Water from three-foot hole dug near west side of valley west of Furnace Creek Ranch.....	2.77	1.75
341	Water from four-foot hole dug about middle of valley due west of Furnace Creek Ranch	15.12	2.38
342	Water from three-foot hole dug near east side of valley, due west of Furnace Creek Ranch	34.18	2.98
343	Water from slough at old bridge, west of Furnace Creek Ranch.....	32.05	2.25

In Table VI are given results of fuller analyses of certain typical brines of this general region. The actual determinations are of potassium chloride and sulfuric acid. The sodium is calculated from the weights of chlorine and sulfuric acid in excess over that required to saturate the potassium. These brines are free from carbonates and contain, if any, at most only traces of calcium and magnesium.

Owens Lake, occupying a depression on the extreme western border of this area, is of interest in view of the fact that its brine has been shown to contain 4.54 per cent. of potassium.¹

¹ Loew, *Ann. Rept. Geol. Surv.*, W. 100 Mer., 1876, p. 190.

This log has been interpreted favorably. On the basis of this interpretation it appears reasonable to believe that the potassic brines of previous ages may have undergone evaporation in this basin, possibly to the point of deposition of potassium compounds, and that such deposits lie buried beneath the accumulations of detrital material now being explored.

In the following table of analyses of brines and saline crusts from Railroad Valley the numbers lacking from the series are those of samples whose total saline content was so low as to make them of slight interest:

TABLE VI—ANALYSES OF CERTAIN BRINES FROM RAILROAD, DEATH, PANAMINT AND DIXIE VALLEYS. RESULTS ARE RECORDED AS GRAMS PER 100 CC. A. R. MERZ, ANALYST

No.	Locality	KCl	NaCl	Na ₂ SO ₄	Total solids by addition	Total solids by determination
12A143	Railroad Valley auger hole bored in north end of flat.....	1.47	12.18	1.28	14.93	15.74
12A154	ditto, hole dug by R. V. Co., north end.. of flat.....	2.24	8.89	0.86	11.99	12.09
338	North end Death Valley, sample mentioned above.....	1.61	25.21	6.56	33.38	33.28
Coop. Lab. lot	Panamint Valley. Collected by S. W. 142-1 Austen.....	0.39	6.44	0.74	7.57	7.80
Coop. Lab.	Death Valley, dug hole near center of valley. Collected by W. G. Luckhardt.....	3.06	25.97	9.71	38.74	40.02
161-1 Coop. Lab. lot	Water from Dixie Valley, Nev.....	4.14	23.38	12.06	39.58	43.47

IV. OTHER BASINS OF SLIGHT IMPORTANCE

In Table VII are recorded analyses of brines from certain undrained lakes of southeastern Oregon.

TABLE VII—ANALYSES OF BRINES FROM SALINE LAKES OF OREGON. POTASH RECORDED AS PER CENT. OF TOTAL SOLIDS. A. R. MERZ, ANALYST

No.	Location	Total solids Grams per 100 cc.	K ₂ O Per cent.
11B9	Water from Summer Lake.....	2.04	1.54
11B49	Alkali Lake, water from middle "lake" or pond on playa.....	11.56	4.08
11B64	Alkali lake. Water from south "Lake".....	17.52	3.59
11B70	Water from Albert Lake.....	4.50	1.79

The brines of the remnant lakes and the salt crusts of the playas of other basins in the northwest and southwest have been examined and, in brief, their salts have been found to be largely non-potassic in composition. In no other instances to date have potassium compounds been found in even remotely commercially interesting amounts.

SOLAR REFINERIES OF THE PACIFIC COAST

When potassium compounds first found employment in the arts and industries, their main sources were kelp, or the ashes of sea weeds, and barilla.¹ Kelp was a sintered mass of potassium, sodium, calcium and magnesium chlorides and carbonates, with which various amounts of sand were intermixed. Generally, during the incineration, interaction had taken place to form silicates. For the preparation of potassium salts this was leached and the lixiviate, after being allowed to settle and filtered, was evaporated for the fractional crystallization of potassium sulfate and chloride. The preparation and treatment of kelp during the early part of the 19th century constituted one of the important industries of the northern British Isles.

Following the development of the market for potash, the extraction of the latter from sea water became

a commercial possibility due to the ingenious method of Balard, as elaborated by Merle and Pechiney.¹ This reached its maximum development at Geraud en Camarque, at the mouth of the Rhone, where it was operated in conjunction with an extensive solar evaporator of ocean brine. The mother liquors from the "salt gardens" were subjected to further treatment by the Balard process for the extraction of potassium chloride. A product of about 80 per cent. purity was obtained. It is estimated that the annual output in potassium chloride from this process was at one time 400 tons per annum. The exploitation of the potassic compounds encountered in the so-called Stassfurt deposits of salts was partially instrumental in bringing about the decline of the kelp industry in Europe and successfully impeded the further development of the industries based on the extraction of potassium chloride from sea water. The value of and ready market for the low-grade potassium compounds, or mixtures, as manure salts for fertilizer purposes should prove an advantage to the latter industry to-day not enjoyed by that industry in its incipency.

The Solar refineries of the Pacific Coast are situated at San Mateo, Mt. Eden and Alvarado, California.

Technology.—The sea water is pumped at high tide into one end of a long series of shallow ponds. These are connected with each other, and as the evaporation proceeds, the brine flows through the series of ponds,

TABLE VIII—ANALYSES OF BITTERNS FROM SEA WATER. R. F. GARDNER, ANALYST

Serial No.	11B 198	11B 199	11B 200	11B 201	11B 202	11B 204	11B 205
K.....	8.2	13.4	13.2	14.6	21.5	35.0	11.8
Na.....	72.6	62.7	60.9	24.5	4.7	93.6	551.1
Ca.....	1.2	2.2	0.6	0.5	1.0	0.2	1.1
Mg.....	24.0	23.4	50.6	62.7	79.4	8.6	43.9
Cl.....	179.2	176.6	179.4	183.3	220.1	180.4	190.8
SO ₄	30.0	31.4	53.6	74.2	62.0	29.0	55.8
Br.....	3.0	2.0	2.0	3.0	2.0	2.0	2.8

* CONVENTIONAL COMBINATIONS

KCl.....	15.6	25.5	25.5	27.8	41.0	66.7	22.5
NaCl.....	184.2	159.1	154.6	62.1	11.9	237.6	129.7
CaCl ₂
MgCl ₂	77.1	84.5	110.8	176.3	256.9	5.8	132.9
Na ₂ SO ₄
CaSO ₄	4.0	7.4	2.3	1.7	3.3	0.6	3.7
MgSO ₄	33.9	39.8	65.0	91.5	75.3	35.8	65.4
MgBr ₂	3.4	3.4	3.4	3.4	2.3	2.3	3.2

DESCRIPTION OF SAMPLES

- 11B 198. Leslie Salt Refining Works, San Mateo, Calif. Mother liquor; representative sample from near northwest corner of mother-liquor pond.
- 11B 199. Leslie Salt Refining Works, San Mateo, Calif. Sample from southeast corner of mother-liquor pond.
- 11B 200. Leslie Salt Works, San Mateo, Calif. Mother liquor from salt-making pond (solar evaporator or "salt garden"); pond has been "making salt" during the summer.
- 11B 201. Oliver Salt Works, Mt. Eden, Calif. Mother liquor from slop pond. Represents an accumulation of 5 years.
- 11B 202. Oliver Salt Works, Mt. Eden, Calif. Mother liquor which has been subjected to some special treatment.
- 11B 204. California Salt Co., Alvarado, Calif. Mother liquor from "slop" pond. Represents about 3 years' accumulation, with the abstraction of considerable quantities for "forcing" purposes and the addition of small quantities of other waste liquors.
- 11B 205. Pioneer Salt Co., San Francisco, Calif. Mother liquor. One year's accumulation.

¹ For a complete bibliography of the literature dealing with kelp and barilla see "Reference List of Papers Concerning the Economic Uses of Algae and Concerning the Salts Derived from Ashes," which is printed as Appen. S. of Senate Document 190, 62nd Congress, 2nd Session, being a preliminary report by the Bureau of Soils on the "Fertilizer Resources of the United States."

¹ For a description of this process, cf. Wurtz, *Hoffman's Ber. II* (1871) *Ausstellung*, [1] 1875, 410; Lunge, *Chem. Ind.*, 1883, 225.

gradually increasing in concentration. Gypsum is deposited during this stage of the process. When the brine has reached a concentration of about 75° or 80° by the salimeter, it is pumped into the so-called lime ponds, and when it approaches saturation (100° by the salimeter), thence into the "salt-making" ponds. Here it is allowed to deposit salt during a summer. At the end of the season, the mother-liquor is run off or pumped off and the crystallized salt is scraped from the bottom of the pond.

The mother liquor is either discarded or is stored in ponds. This is used at times to increase the concentration of brines which have not reached a high enough concentration to deposit salt. The approach of the end of the season, rather than the concentration of the impurities in the mother liquor, is the determining factor in bringing the evaporation to a close.

The mother liquors contain, in addition to their saline constituents, a considerable amount of organic matter consisting of bacteria, the larvae of a certain fly, and the disintegrated remains of fish. The color of the mother liquors is red.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

RECENT ANALYSES OF THE SARATOGA MINERAL WATERS. II.

By LESLIE RUSSELL MILFORD
Received October 8, 1912

IN THIS JOURNAL, 4, 593, was published the first of the series of analyses which are being made for the Saratoga Reservation Commission by the State Department of Health.

The analytical data published showed that those springs were four of the most highly mineralized in the reservation. They are strongly alkaline-saline waters having a large excess of sodium chloride and a high calcium and magnesium bicarbonate content.

Since this first paper was written several more analyses of the various springs have been made. The results which are given below show that these springs are less mineralized than the four previously published and are representative of the milder saline-alkaline class.

Many of these saline-alkaline waters of Saratoga differ from each other, for all practical purposes, merely in the degree of concentration of their mineral substances. The investigation has shown that the mineral water basin is relatively large and waters of diverse mineralization are found, but all have general and characteristic constituents. Some of the most valuable waters are so similar throughout, or the gradations are so finely shaded off that the choice between them becomes a personal factor. The strongest waters have a strong purgative or cathartic and diarrhetic action on the system, while the less highly mineralized become of relatively mild therapeutic effect, but are valuable and useful table waters. The waters of which the analyses are here given are used partly for drinking and partly for bathing.

The pumping of the waters for the gas contained in them has been stopped and the springs are rapidly

increasing in flow, mineralization, and carbon dioxide content.

Sanitary improvements have been made and the physical conditions have been altered at many of the springs. Some have been cleaned, some retubed, some capped and some fitted with a water column to give a hydrostatic head, thus preventing a wasteful flow of the water and exhaustion of the other springs. The depleted mineral water basin is rapidly restoring itself and the ground water is approaching its normal level. This fact is shown by the revival of many of the springs that had ceased to flow and the increase in the volume of those that were already flowing. In the Geyser Park district the famous Geyser Spring has become active and is now throwing a stream of water seven and one-half (7½) feet above the surface of the ground. Two other "spouters" have recently been discovered which throw large streams of water accompanied by great volumes of gas nearly seventeen (17) feet into the air. Such conditions give very promising results and prove the wisdom of having unified ownership of the springs, cessation of pumping the waters for gas, and the conservation of most interesting and valuable group of springs in the world. Experiments and research work are now being conducted to find a spring water suitable for bottling and use as a table water. The results will be given in another paper.

Whenever it was possible to obtain an advertised analysis, or analytical data from a previous published report, these have been inserted. Many of these older analyses were reported in grains per U. S. gallon, but the writer has re-calculated them to a uniform basis of milligrams per liter and re-stated as ions.

The hypothetical compounds have been calculated also from these ions to conform to the scheme adopted by the United States Department of Agriculture and followed by the State Health Department.

The analyses which follow give the comparisons of the mineral content of the springs when analyzed at various dates by other analysts and the recent work of the writer.

DESCRIPTION OF THE SPRINGS

The Peerless Spring is opposite the famous High Rock and was discovered in 1887. It is one hundred and fifty (150) feet deep and flows freely at the surface of the ground. The water is highly charged with carbon dioxide gas and is suitably mineralized, making a very popular and palatable drinking water. It contains the same general chemical compounds that exist in all of the Saratoga waters, principally, sodium chloride, calcium, magnesium and sodium bicarbonates. Free service is maintained throughout the year, and the public have availed themselves of the opportunity to drink the water. The surplus water is used in the Magnetic bath house.

Situated about ten (10) feet from the Peerless is the Magnetic Spring which illustrates the fertility and diversity of Saratoga's mineral water resources. This spring was discovered in 1873 and is fifty (50) feet deep. The waters of this spring are moderately mineralized and, like the Peerless, contain the important constituents, sodium chloride, calcium, magnesium and sodium

CONSTITUENTS AS ACTUALLY DETERMINED

DATE OF ANALYSIS	PEERLESS SPRING			MAGNETIC SPRING			EMPEROR Before retubing	SPRING After retubing	PUTNAM SPRING		PATTERSON SPRING	
	1	2	3	4	5	6	7	8	9	10	11	12
	RESULTS IN MILLIGRAMS PER LITER											
	Nov. 7 1887	Aug. 12 1905	Jan. 22 1912	Dec. 7 1886	Aug. 12 1905	Feb. 7 1912	Feb. 26 1912	June 19 1912	—1891	April 10 1912	April 1888	May—21 1912
Formula	IONS, RADICLES, AND OXIDES DETERMINED											
SiO ₂	16.95	14.80	11.80	6.27	42.70	50.75	30.15	13.15	39.84	20.75	17.44	13.50
SO ₄	11.71	4.00	21.42	trace	2.30	10.09	35.23	3.30	7.07	96.50	4.15	92.80
HCO ₃	2892.97	2634.40	2887.65	1822.23	1816.80	1491.93	1419.21	2431.21	2612.20	1394.80	3285.28	1211.70
NO ₃	a	none	none	a	trace	trace	trace	0.09	a	trace	a	1.77
NO ₂	a	trace	trace	a	trace	trace	0.04	trace	trace	trace	a	trace
PO ₄	trace	none	none	a	none	none	none	none	a	none	a	none
AsO ₄	a	none	none	a	none	none	none	none	a	none	a	none
BiO ₂	trace	trace	trace	a	trace	trace	trace	trace	a	trace	trace	trace
Cl ₂	2046.51	1773.10	1624.43	781.28	1313.40	669.93	725.88	1594.74	2204.28	619.46	2896.70	438.10
Br.....	16.08	16.80	9.55	0.78	11.80	4.91	4.43	11.59	17.25	8.87	8.93	4.09
I.....	0.06	1.00	0.85	a	0.30	0.31	0.31	0.38	1.20	0.15	2.18	0.31
Fe.....	7.40	a	11.47	0.16	a	16.00	10.91	4.28	5.81	10.29	6.49	6.19
Fe and Al.....	8.76	5.60	17.09	2.61	97.80	16.60	12.71	10.00	6.81	10.45	6.91	7.57
Al ₂ O ₃	2.52	a	10.61	4.63	a	1.10	3.40	10.79	1.88	0.30	0.80	2.61
Mn.....	a	none	trace	a	none	none	none	trace	7.34	trace	2.56	none
Ca.....	500.86	530.40	528.88	366.22	326.40	269.10	296.90	511.01	461.91	421.57	546.44	231.57
Mg.....	156.40	90.90	162.13	98.80	122.80	84.50	83.20	145.73	177.79	89.04	251.32	63.75
Ba.....	a	2.10	2.94	trace	4.40	3.50	1.30	1.29	10.22	0.47	trace	trace
Sr.....	a	none	trace	a	trace	trace	0.20	trace	a	0.19	trace	trace
K.....	104.04	94.70	112.93	72.02	56.90	34.55	39.68	110.25	26.38	64.08	110.17	48.24
Na.....	1398.27	1298.50	1152.00	539.83	849.70	487.98	482.73	1005.04	1519.01	474.97	1906.77	356.33
Li.....	2.26	0.44	0.80	0.36	3.20	1.73	1.27	4.12	2.44	1.10	4.09	2.28
NH ₄	3.17	5.88	3.78	a	3.42	2.79	2.75	3.97	a	2.36	* 7.80	1.40
Oxygen to form Al ₂ O ₃	1.18	4.99	2.18	0.50	1.60	5.07	0.88	0.10	0.38	1.23
Oxygen to form Fe ₂ O ₃	24.00
Oxygen to form Mn ₂ O ₃	2.84	0.99
F.....	trace	trace
Organic matter.....	trace
HYPOTHETICAL FORM OF COMBINATION												
NH ₄ Cl.....	9.40	17.46	11.22	a	10.16	8.27	8.17	11.77	a	6.99	23.02	4.15
LiCl.....	13.70	2.64	5.20	2.19	19.40	10.63	7.67	24.94	14.79	7.10	24.76	13.82
KCl.....	183.24	164.50	206.33	136.63	97.50	61.31	71.55	198.70	34.00	114.22	200.11	88.18
NaCl.....	3199.91	2771.60	2495.83	1177.35	2051.30	1032.31	1120.69	2429.03	3585.65	913.83	4545.67	629.32
KBr.....	24.02	25.00	14.00	1.15	17.50	7.20	6.50	17.00	25.29	13.00	13.49	6.00
KI.....	0.07	1.30	1.12	a	0.40	0.40	0.40	0.50	1.71	0.20	2.85	0.40
Na ₂ SO ₄	17.33	5.90	31.67	trace	3.40	14.95	52.15	4.88	10.45	142.85	6.13	137.37
NaNO ₃	a	none	none	a	trace	trace	trace	0.12	trace	trace	a	2.42
NaNO ₂	a	trace	trace	a	trace	trace	0.06	trace	a	trace	a	trace
NaBO ₂	trace	trace	trace	a	trace	trace	trace	trace	a	trace	trace	trace
NaHCO ₃	490.67	752.30	585.31	280.87	151.20	281.85	91.76	169.83	385.95	252.95	455.37	232.36
Ba(HCO ₃) ₂	a	3.90	5.56	trace	8.30	6.62	2.50	2.44	19.32	0.89	trace	trace
Sr(HCO ₃) ₂	a	none	trace	a	trace	trace	0.50	trace	a	0.45	trace	trace
Mg(HCO ₃) ₂	949.33	547.30	984.13	599.73	739.30	512.90	505.00	884.58	1079.18	540.23	1525.15	386.69
Ca(HCO ₃) ₂	2228.49	2148.10	2141.96	1483.25	1321.90	1090.00	1202.40	2069.59	1870.74	978.36	2213.08	937.87
Fe(HCO ₃) ₂	23.60	17.80	36.47	0.51	132.90	50.88	34.70	13.61	18.47	32.72	20.69	19.68
Mn ₂ O ₄	a	a	trace	a	a	none	none	trace	10.18	trace	3.55	none
Al ₂ O ₃	2.52	a	10.61	4.63	{ 80.00 }		1.10	3.40	10.79	1.88	0.30	2.61
Fe ₂ O ₃	10.57	a	a
SiO ₂	16.95	14.80	11.80	6.28	42.70	50.75	30.15	13.95	39.84	20.75	17.44	13.50
Total solids in solution (computed).....	7159.23	6472.60	6541.21	3692.58	4675.96	3129.17	3137.60	5851.73	7097.46	3024.84	9052.11	2474.64
Residue on evaporation dried at 105° C.....	a	a	4880.00	a	a	2288.00	2398.00	4696.00	a	2188.00	a	1768.00
Temperature.....	a	a	9.5° C.	a	a	11.1° C.	9.6° C.	10.0° C.	10.55° C.	11.1° C.	a	10.3° C.

11. Chandler & Fellow—Hydrotherapy at Saratoga by J. A. Irwin, 1892.
5. Mineral Waters of the U. S. U. S. Dept. of Agriculture, Aug. 12, 1905.
- 3, 6, 7, 8, 10, 12. Files N. Y. State Dept. of Health, 1912.
4. Samuel Duffield Hydrotherapy at Saratoga by J. A. Irwin, 1892.
9. Maurice Perkins

a. Not given.

Other References:

Advertised analyses in various circulars.

Therapeutic Saratoga—American Medical Association, June, 1902.
"Mineral Waters of the U. S. and their Therapeutic Uses," J. K. Crook, 1899.

bicarbonates. This spring has a wide reputation for bathing for the cure of rheumatism, gout and skin diseases. There has been nothing found in analyzing the water from this spring which would account for its name, "Magnetic." The spring is an artesian well with an iron casing driven into the earth. The phenomenon of magnetism is exhibited principally in at-

tracting small objects to the iron casing, the clinging of a steel tape to the tubing when measuring the depth of the well and the deflection of the magnetic needle in the vicinity. The belief is that the phenomena are induced by earth magnetism, aided by the rise and fall of the drill inside of the iron casing, producing sharp vibrations which tend to facilitate the

readjustment of the polarized particles of iron and their orientation to the direction of earth magnetism at that point.¹

When, after the drill is magnetized, it is repeatedly passed (in the process of drilling) up and down through the casing in the same position and direction of movement, it gradually imparts its magnetism to the casing. Sometimes in driving the casing, by means of a heavy weight, vibrations are set up much the same as those in the drill and induce more or less magnetism.

Opposite the Peerless and Magnetic Springs and about one hundred (100) feet south of the celebrated High Rock, is situated the Emperor Spring. This spring was cleaned and retubed to a depth of 117 feet in April and gives a water twice as strongly mineralized as the water showed before retubing. It is just back of this spring where the escarpment of the geological fault, which gave birth to the mineral springs, is best displayed.

This rocky cliff is now exposed as the buildings with their attendant refuse and rubbish heaps, which formerly concealed it, have been removed. The water of the Emperor Spring flows freely at the surface of the ground and resembles very closely that of the Peerless. It has a good supply of gas and is suitably mineralized.* The water is drunk at the spring, free service being maintained. The excess or overflow from the bowl is piped across the road to the Magnetic bath house, where it is used for bathing.

The Putnam Spring was discovered in 1890 and is about 200 feet deep. This was known as the Levingston Spring and is north of the Patterson Spring and separated from it by Phila Street. This Spring is situated in the Congress Park group and belongs to the milder class. The Putnam has not been exploited commercially, except in connection with the mineral water baths at the Levingston bath house, which stands upon the same lot and under which the waters of the spring emerge. This spring does not flow at the surface of the ground, so the sample for analysis was obtained by pumping. The analysis is given for its scientific interest and completeness of the series. The water is high in sulfates. It is not used at the bath house at present, as an arrangement has been made whereby the surplus water from the Hathorn Spring No. 1 is pumped to the baths and used for bathing.

A few feet south of the Putnam Spring is the Patterson Spring. This Spring was discovered in 1888 and is 250 feet deep, 190 feet being through solid rock. This spring is in the Congress Park area on property north of and adjoining the Hathorn Spring No. 1. Its relations to the latter spring are intimate, as have been shown in recent experimental work on the pumping of this spring and noting the effect on the mineral content, flow, and other physical conditions of the Hathorn No. 1. This water is also high in sulfates and is very similar to the Putnam.

The waters of the Patterson have been deemed valuable for certain disorders of the human body, but they have not had the reputation of some of the other

waters. The Patterson used to appear on the market as a bottled water, but the spring is not being exploited now.

SANITARY ANALYSES

In order to insure the wholesomeness and purity of the waters, sanitary and bacteriological analyses of the springs have been made from time to time. The sanitary analyses have shown small amounts of free and albuminoid ammonia, low nitrates, and nitrites.

The bacteriological examinations showed a very low count and absence of *B. Coli*, which indicates high sanitary purity.

STATE HYGIENIC LABORATORY
STATE DEPARTMENT OF HEALTH
ALBANY, NEW YORK

THE QUANTITATIVE SEPARATION OF MIXTURES OF CERTAIN ACID COAL TAR DYES¹

By W. E. MATHEWSON

Received January 22, 1912

INTRODUCTION

The use of immiscible solvents for separating mixtures of acid coal tar colors is discussed in most standard works on the subject. Loomis² gives data concerning the solubility of a large number of common dyes, and Seeker³ has published qualitative separations of Orange I and Naphthol Yellow S from certain other dyes depending on the use of amyl alcohol. In such procedures any variation made in the acidity has been attained by using acids of different degrees of dissociation, as acetic acid and a mineral acid, and not by adding varying amounts of the same acid. Chiefly with the object of making a quantitative separation of the colors permitted in foods (Naphthol Yellow S, Ponceau 3 R, Orange I, Amaranth, Light Green SF Yellowish, Erythrosin and Indigo Carmin),⁴ their ratios of distribution between dilute hydrochloric acid of different concentrations and certain immiscible solvents were determined.⁵ The data indicated a method that gives good results in practice and is of quite general applicability. Some figures have also been obtained for other similar colors that will show where separations can be made and can also be applied for qualitative differentiations.

DATA OBTAINED

In the accompanying table the figures given show the percentage of color remaining in the aqueous layer after shaking with an equal volume of the immiscible solvent. A solution containing a quantity of dye equivalent to 0.1000 gram of pure color was diluted to 50 cc. with water and standardized hydrochloric acid, sufficient of the latter being taken to give the solution exactly the acid normality desired. It was then shaken out with 50 cc. of the solvent. (This shaking was continued for five minutes with dichlorhydrin, two minutes with the other solvents.)

¹ Published by permission of the Secretary of Agriculture.

² U. S. Dept. Agr., Bureau of Chemistry, *Circ.* 63.

³ "Allen's Commercial Organic Analysis," 4th Ed., Vol. V.

⁴ U. S. Dept. Agr., Office of the Secretary, Food Inspection Decision 76.

⁵ Distribution ratios of the permitted dyes between dilute hydrochloric acid and amyl alcohol were sent out by the writer in April, 1911, in a circular letter in connection with the cooperative work of the Association of Official Agricultural Chemists.

¹ Underground Water Papers 1910. U. S. Geological Survey Water Supply Paper 258.

TABLE I.—PERCENTAGE OF COLOR IN THE WATER SOLUTION AFTER SHAKING WITH AN EQUAL VOLUME OF IMMISCIBLE SOLVENT

SOLVENT: AMYL ALCOHOL	Normality of hydrochloric acid in water layer before shaking								
	4	2	1	1/2	1/4	1/8	1/16	1/32	
COLORS	Percentage of color in water solution after shaking								
Naphthol Yellow S No. 4..	4	7	11	17	27	43	
Orange I No. 85.....	0.5	1	2	4	
Ponceau 3 R No. 56.....	1	3	7	21	43	64	78
Amaranth No. 107.....	5	15	52	82	93
Light Green S. F No. 435..	90	95	97	99	99
Erythrosin No. 517.....	0
Indigo Carmin No. 692....	34	51	89	96	99
Fast Yellow No. 8.....	36	..	61
Crocein Orange G No. 13..	1	2	..
Orange G No. 14.....	18	..	58
Ponceau 2 R No. 55.....	..	2	..	14
Crystal Ponceau No. 64..	8	..	39
Fast Red B No. 65.....	2	..	16	..	62
Resorcin Yellow No. 84..	5	..	11	17	..
Orange II No. 86.....	2	3	..
Brilliant Yellow S No. 89.	73	..	90
Tartrazin No. 94.....	47	..	88
Metanil Yellow No. 95....	1	1	..
Fast Red A No. 102.....	0.2	1	..
Fast Red C No. 103.....	1	..	4
Fast Red E No. 105.....	1	..	17	..	68
New Coccin No. 106.....	15	..	75
Scarlet 6 R No. 108.....	41	80	95
Resorcin Brown No. 137..	8	..	20
Cotton Scarlet 3 B No. 146.	2	..	10
Congo Red No. 240 ¹
Azo Blue No. 287 ²
Chrysophenin No. 329....	1	2	..
Guinea Green B No. 433..	48	..	32	..	25
Acid Magenta No. 462....	75	..	93
SOLVENT: DICHLORIN.									
Naphthol Yellow S No. 4..	15
Ponceau 3 R No. 56.....	37
Orange I No. 85.....	4
Amaranth No. 107.....	95
Light Green S F No. 435..	15	..	17
Indigo Carmin No. 692....	91
Acid Magenta No. 462....	86
SOLVENT: AMYL ACETATE.									
Naphthol Yellow S No. 4..	22	33	48
Ponceau 3 R No. 56.....	95	96	97
SOLVENT: ETHER.									
Naphthol Yellow S. No. 4..	..	94	97
Orange I No. 86.....	..	97	97

¹ Color acid nearly insoluble in both layers.² Similar to Congo Red but color acid more soluble in alcohol.

After separation of the liquids, which takes place very rapidly with strongly acid mixtures but more slowly with low acid concentrations, the lower layer was drawn off and the percentage of dye remaining in the water layer estimated. All color determinations were made by Knecht and Hibbert's method,¹ a standard solution of pure amaranth being used to titrate back any excess of titanium chlorid added. The extractions were made at room temperature, 27° to 30° C.

Of the coloring matters used, the permitted colors were from analyzed commercial samples of excellent grade. The others were commercial samples of good quality, their examination, however, being limited in most cases to a determination of total color and a comparison of their reactions with the description given in Heumann and in Schultz and Julius (translated and enlarged by A. G. Green, 1904). The serial numbers used in the latter work are given with the names of the dyes.

¹ New Reduction Methods in Volumetric Analysis, 1910.

DISCUSSION OF RESULTS

In applying the data given in the table for effecting the quantitative separation of two colors the following procedure, or some simple modification of it, has been practiced: The solution containing 0.2 to 0.4 gram of color (depending on the nature of the dyes) is treated with sufficient water and hydrochloric acid of known strength to bring its volume to about 50 cc. and its acid concentration to that point for which the difference in percentage of color extracted for the two dyes is near its maximum. The solution is then shaken out with the immiscible solvent, being passed in succession through three or four separatory funnels each containing 50 cc. of the latter. The portions of the solvent are washed with 50 cc. of hydrochloric acid of the same normality as the solution, being passed successively through the separatory funnels in the same order as was the original solution, and this operation is repeated with one or two fresh amounts of the hydrochloric acid. The dye relatively more soluble in water is determined in the combined washings and extracted solution. The second dye is removed from the solvent by shaking with water, very dilute caustic soda, or, more quickly, with dilute caustic soda after the addition of some gasoline, or similar substance in which the color is insoluble.

Assuming the distribution ratios to remain constant, this procedure using four funnels and making three washings gives for a pair of colors whose "distribution numbers" (as the percentage numbers given in the table may be called) are 80 and 20, respectively, a separation of 98.30 per cent. for each color. With distribution numbers 90 and 10 four funnels and three washings give a calculated separation of 99.73 per cent., and the same is obtained with distribution numbers 81.8 and 5.3 if the solvent in which the dyes are relatively more soluble be taken in portions one-half the volume of those of the other liquid. If the second, third, and fourth funnels be given a fifth washing, the third and fourth funnels a sixth, and the last funnel a seventh washing, the calculated loss for the color more soluble in the solvent layer is 0.76 per cent., while the percentage of the other dye removed is relatively much increased (to 99.99 per cent.). In most mixtures the progress of the separation is always apparent.

In practice, because of incomplete extraction and separation, and especially on account of uncertainty due to small amounts of subsidiary dyes always present, it is necessary to increase the number of successive extractions. The distribution ratios change somewhat with varying dye concentrations, the color being relatively more soluble in the non-aqueous layer at very high dilutions. The formation of esters of the color acids is a possible source of difficulty, but it is not believed to take place. With amyl alcohol as solvent it is almost always desirable to make the original solution more strongly acid than is indicated by the distribution data and use relatively more portions of the washing liquid.

Of the permitted colors, Naphthol Yellow S is best

separated from Orange I by washing the amyl alcohol solution of the color acids with strong salt solution, care being taken that not too much color is present. With a solution containing 20 grams of salt and 0.04 gram Naphthol Yellow S per 100 cc. and shaken with an equal volume amyl alcohol, 97 per cent. of the color is retained by the water. With a similar solution containing 0.07 gram Orange I, the water layer contains 1.5 per cent. of the total color. With higher concentrations some color may be salted out in solid form, but this does not interfere if the amount is small. Erythrosin being quantitatively removed from slightly acid solutions by amyl acetate, ether, or amyl alcohol, its separation from sulphonated colors presents no difficulty.

ANALYSES OF MIXTURES

Analyses of a number of mixtures were made with the following results. In all cases the last washings were free or practically free from colors. As the determination of total color is convenient and accurate, it was in most cases made, together with that of the dye reacting with the lesser amount of titanium trichlorid.

NAPHTHOL YELLOW S AND LIGHT GREEN S F YELLOWISH

Twenty cc. of a solution containing, in this volume, 0.1000 gram green and 0.1083 gram yellow was treated with 20 cc. five-normal hydrochloric acid and diluted to 50 cc., then shaken out with three portions of amyl alcohol of 50 cc. each. The amyl alcohol was washed with two portions (50 cc. each) of two-normal hydrochloric acid. Green was determined in the extracted solution and washings, total color in another aliquot of the original solution.

Green, found 0.0975 gram = 97.5 per cent.

Yellow, found 0.1085 gram = 100 per cent.

NAPHTHOL YELLOW S, ORANGE I, AND INDIGO CARMIN

Thirty cc. of solution containing 0.1000 gram orange, 0.1000 gram blue, and 0.1083 gram yellow was treated with 2 cc. five-normal hydrochloric acid and shaken through three funnels containing each 60 cc. amyl alcohol. The latter was, then washed with two portions of dilute hydrochloric acid (2 cc. five-normal hydrochloric acid + 28 cc. water, or one-third normal). The second and third funnels were then washed with a third portion of acid (30 cc.) and the third funnel with a fourth portion. The blue was determined directly in the extracted solutions and washings.

The amyl alcohol was then washed with four portions of 120 cc. each sodium chlorid solution (200 grams per liter). The second and third funnels were washed a fifth time and the third a sixth time.

Blue, found 0.099 gram = 99 per cent.

Orange, found 0.0985 gram = 98.5 per cent.

Total color was determined and yellow estimated by difference.

Yellow, found 0.1080 gram = 99.5 per cent.

PONCEAU 3 R AND NAPHTHOL YELLOW S

Twenty cc. of solution containing 0.1083 gram yellow and 0.1162 gram Ponceau was treated with 20

cc. concentrated hydrochloric acid and passed through four funnels containing each 60 cc. of amyl acetate. The amyl acetate portions were washed with 3 portions of 30 cc. each of four-normal hydrochloric acid, a fourth washing given to the last three funnels, a fifth to the last two, and a sixth to the last one. From the extracted solution and washings, the Ponceau was taken up with amyl alcohol, the latter diluted with gasoline, the color removed with dilute caustic soda and determined. Total color was determined and yellow estimated by difference.

Ponceau, found 0.1132 gram = 97 per cent.

Yellow, found 0.1089 gram = 100.5 per cent.

AMARANTH AND ORANGE I

Twenty cc. of solution containing, in this volume, 0.1000 gram orange and 0.1723 gram Amaranth was treated with 2 cc. five-normal hydrochloric acid and 28 cc. water and passed through two funnels containing 50 cc. each of amyl alcohol. The latter were then washed twice with 50 cc. volumes of eighth-normal hydrochloric acid. Amaranth was determined directly in the extracted solution and washings. Total color was determined in an aliquot of the original solution.

Amaranth, found 0.1731 gram = 100.5 per cent.

Orange, found 0.0995 gram = 99.5 per cent.

LIGHT GREEN S F YELLOWISH, AMARANTH, PONCEAU 3 R, AND ORANGE I

Thirty-seven cc. solution containing, in this volume, 0.1000 gram green, 0.1000 gram Ponceau, 0.1000 gram orange, and 0.1162 gram Amaranth was treated with 20 cc. of concentrated hydrochloric acid and shaken through three funnels containing each 50 cc. amyl alcohol. The latter was washed with three portions (50 cc.) of four-normal hydrochloric acid. Green was determined in the extracted solution and washings.

Two more funnels containing 50 cc. portions of amyl alcohol were now added and the series washed with five 50 cc. amounts of fourth-normal hydrochloric acid. The first washing was colorless on coming from the fourth funnel and was discarded. The second, third, fourth, and fifth funnels were given a sixth additional washing, the last three a seventh, the last two an eighth, and the last one a ninth. The extracted solution and washings were combined, nearly neutralized with two-normal ammonium hydroxid, evaporated to about 150 cc., and Amaranth determined.

A second portion of 37 cc. of the original solution was treated with 2 cc. of five-normal hydrochloric acid and made up to 75 cc., then shaken out with four 25 cc. portions of amyl alcohol. These were washed with five portions (75 cc. each) sixteenth-normal hydrochloric acid. The last three funnels were given a sixth washing, the last two a seventh, and the last one an eighth. Each of the last three amyl alcohol portions was diluted with 10 cc. of light gasoline before shaking out with its final portion of washing liquid. After further addition of gasoline, the orange was removed with dilute caustic soda, and estimated. Total color was determined in an aliquot of the origi-

nal solution and the Ponceau found by difference.¹

Green, found 0.098 gram = 98 per cent.

Amaranth, found 0.116 gram = 100 per cent.

Orange, found 0.102 gram = 102 per cent.

Ponceau, found 0.098 gram = 98 per cent.

PONCEAU 3 R AND INDIGO CARMIN

Twenty-eight cc. of solution containing 0.1000 gram Ponceau and 0.1000 gram blue was treated with 2 cc. five-normal hydrochloric acid and shaken with four 50 cc. portions of amyl alcohol. Three portions (50 cc. each) of third-normal hydrochloric acid were then passed through the series of funnels, a fourth washing given to the last three, a fifth to the last two, and a sixth to the last one. Blue was determined directly in the extracted solution and washings. Total color was estimated and the Ponceau obtained by difference.

Blue, found 0.102 gram = 102 per cent.

Ponceau, found 0.099 gram = 99 per cent.

LIGHT GREEN S F YELLOWISH AND INDIGO CARMIN

Twenty-three cc. solution containing 0.1000 gram blue and 0.1000 gram green was treated with 2 cc. five-normal hydrochloric acid and shaken out with six 25 cc. portions of dichlorhydrin (saturated with water). The dichlorhydrin portions were passed successively through four funnels containing each 25 cc. of fourth-normal hydrochloric acid saturated with dichlorhydrin. They were then combined, diluted with benzol, the color removed with water, and titrated. Total color was determined and blue found by difference.

Green, found 0.099 gram = 99 per cent.

Blue, found 0.101 gram = 101 per cent.

NAPHTHOL YELLOW S AND AMARANTH

A 10 cc. solution containing 0.1273 gram Amaranth and 0.1083 gram yellow was treated with an equal volume of concentrated hydrochloric acid and shaken through three funnels each containing 40 cc. amyl acetate. The amyl acetate portions were then washed with 20 cc. of six-normal hydrochloric acid and the last two funnels given a second washing. The Amaranth was determined in the extracted solution and washings. The Naphthol Yellow S was removed from the amyl acetate by washing with a little dilute caustic soda solution and determined directly.²

Amaranth, found 0.128 gram = 101 per cent.

Yellow, found 0.108 gram = 100 per cent.

In using the table to distinguish qualitatively between such colors as Amaranth and the other fast reds, or Guinea Green and Light Green S F Yellowish,

¹ The separation of Orange I from Ponceau 3 R by means of hydrochloric acid and amyl alcohol alone gives high results for the orange, due to the fact that the distribution ratio of the Ponceau changes rather markedly with varying dye concentration; Instead of the procedure given above, involving the use of gasoline, the Amaranth, green, and most of the Ponceau may be removed with sixteenth-normal acid, and the remainder of the Ponceau with five per cent. sodium chloride solution. Four funnels are required. Four washings are given with the hydrochloric acid, then three with 5 per cent. salt, and the last funnels washed with one, two, and three additional amounts of salt solution, respectively. Amyl alcohol, acid, and salt solution are taken in 50 cc. portions, and the amount of Orange I present should not exceed 0.04 g.

² Naphthol Yellow S is conveniently titrated in tartrate solution, a little Light Green S F Yellowish being added to serve as indicator.

it must be remembered that the relative intensity of the coloration of the two layers is usually somewhat different from their relative concentration and may be very much so.

NEW YORK FOOD AND DRUG INSPECTION LABORATORY

THE ALCOHOL REQUIREMENT OF THE PURE FOOD AND DRUG LAW AND THE ACCURACY OF ALCOHOL ASSAYS OF PHARMACEUTICAL PREPARATIONS

By C. H. BRIGGS

Received Aug. 19, 1912

Before the Pure Food and Drug Law went into effect it is doubtful if manufacturing pharmacists paid very much attention to the accurate determination of the alcohol in their preparations. They were in position to know how much alcohol went into each preparation and whether this amount of alcohol could be actually recovered was a matter of little moment. However, on the advent of the Pure Food and Drug Law, it became necessary to state on the label the percentage of alcohol in every preparation, and the problem of determining this exactly began to assume serious proportions. It is doubtful if the framers of the Pure Food and Drug Law had any thought of requiring a statement of the alcohol content of ordinary galenicals such as are put out by the manufacturing pharmacist, but it is probable that their real intention was to require the alcohol content of those medicines sold directly to the laity. In order to do this it was necessary to include all pharmaceutical preparations containing alcohol.

The first interpretation of the Law, that the maximum amount of alcohol could be stated on the label, was a very practical one and did not cause any undue hardship to pharmaceutical manufacturers. It was only necessary to know the amount of alcohol which went into an elixir, or in case of a fluid extract the amount which was usually obtained, to be able to fix upon a maximum percentage for a label claim which would not only be safe from the manufacturers standpoint but would also not deviate excessively from the actual alcohol content.

The later belief, however, that the actual percentage of alcohol must be stated on the label, is a matter of grave concern to the manufacturing pharmacist. To meet this requirement two courses are open:

1. To assay every preparation for alcohol and stamp the actual content on the label.
2. To have the label printed with a standard content of alcohol for each preparation and to adjust each individual lot to the standard.

The first method requires the special stamping of every bottle and is expensive. It also shows variation in the alcoholic content in the individual lots of a preparation which is apt to cause distrust on the part of the pharmacist and require an undue amount of explanation on the part of the manufacturer. Anyone who has had anything to do with the manufacture of fluid extracts, for example, knows that it is impossible to make several lots of the same kind

and have the finished fluids contain the same percentage of alcohol. Variations in the amount of moisture and extractive in the drug, and slight variations in conditions and amount of alcohol lost, all tend to cause considerable variation in the alcohol content of the resulting fluid extracts. Hence, in order to make a fluid extract contain a standard content of alcohol, it is necessary to assay it for alcohol and finally adjust it to the standard by the removal or addition of alcohol. It is also advisable to assay the fluid extract again after it has been adjusted, for the adjusting of a large lot of fluid extract to within 1 per cent. of alcohol is not an easy matter and considerable variations are liable to occur. With this fact in view, the question naturally arises, how accurately can pharmaceutical preparations be assayed for alcohol?

In making alcohol assays there are several sources of error:

1. *Measuring the Sample.*—An error of 0.25 cc. on a 25 cc. sample means that a 90 per cent. alcohol will test 89 per cent. and a 50 per cent. alcohol only 49.5 per cent. An error of 0.1 cc. in measuring the sample means that a 90 per cent. alcohol will test 89.6 per cent. and 50 per cent. alcohol 49.8 per cent. Then there is another similar error in adjusting the distillate to the definite volume required for taking the specific gravity.

2. *Loss of Alcohol on Distillation.*—There seems to be a slight loss of alcohol on distillation, due perhaps to a slight absorption of alcohol around the stoppers or a slight retention of alcohol in the flask and residue. It is not possible to recover all the alcohol from a liquid of more than 50 per cent. strength unless it is diluted with water and double the amount of distillate is collected. This multiplies the error in the specific gravity by two and so increases the error. We have tried adding sodium chloride to the alcohol solution in the flask before distilling but it does not seem to affect the results.

3. *Error in Taking Specific Gravity.*—An error of 1 point in the fourth place or say 0.9541 instead of 0.9540 means an error of about 0.2 per cent. alcohol and an error of 2 points in the fourth place means an error of 0.4 per cent. alcohol.

The Westphal balance is not sensitive to better than 1 point in the fourth place and it requires careful work to get it that closely. The pycnometer method is more accurate but requires a much longer time, which is a very important consideration where a large number of determinations have to be made.

4. *Temperature of Solution when Taking Specific Gravity.*—This may cause considerable error and this point must be watched very carefully.

5. *Essential Oils.*—Essential oils are used in most elixirs and in many compound fluids and tinctures. Small quantities of essential oils distil over with the alcohol and water and dissolve in the distillate. This may increase the specific gravity and lower the alcohol results. Several experiments were tried to see what effect the addition of 1 per cent. of essential oil would have on the assay of 50 per cent. alcohol.

It was found that in a series of nine determinations the results were low from 0.9 per cent. to 1.4 per cent. alcohol.

The effect of drug extracts on alcohol assays was also determined. A quantity of the drug extract was placed in the distilling flask with the usual amount of an alcohol solution of known strength and the assay made in the usual way. The results were as follows:

	ALCOHOL		
	Per cent	Per cent.	Per cent.
Alcohol used	49.7	51.25	56.8
Found by distillation	49.0	50.66	56.14
With extract Cascara Sagrada	48.66	50.16	56.8
With extract Gentian	49.0	49.68	55.4
With extract Belladonna	48.82	50.00	55.51

From this table it will be seen that while the results are about 0.65 per cent. low without the drug extracts, that the average loss of alcohol is about 1 per cent. when the drug extracts are present. Some of the alcohol is apparently held mechanically by the extractive matter.

The writer has had occasion to observe the results of 25 to 30 alcohol assays per day for three or four years, and while there is little doubt that one or a dozen alcohol assays can be made which will not vary more than 0.2 per cent. or 0.3 per cent. when great care is used, still in the regular assay of a great many samples much larger errors will creep in and results may be off as much as 1 per cent. or 1.5 per cent. alcohol. When we stop to consider that an error of 1 per cent. in the alcohol assay of a single lot of 500 gallons of elixir means the addition of 5 gallons of alcohol, worth thirteen dollars, it is really a matter of considerable importance to the manufacturer.

The question now arises, how closely will pharmaceutical preparations have to be adjusted to the label claim to be satisfactory under the Pure Food and Drug Law? This is a difficult question to answer. The rule in force in this laboratory is that all products must assay within 1 per cent. of the alcohol standard on the label before they are accepted.

It is evident, however, that there are several large pharmaceutical manufacturers who are labeling their preparations with statements of the maximum content of alcohol, but it is an open question whether this will satisfy the requirements of the official board.

The writer believes that a ruling to the effect that fluid extracts and elixirs could be labeled with the maximum content of alcohol would be just and fair and would not in any way deflect the real intent of the Drug Law. It would certainly be a welcome measure to pharmaceutical manufacturers who are putting forth their best efforts to conform to the law.

SCIENTIFIC DEPT., PARKE, DAVIS & Co.
DETROIT, MICH.

THE MINERALOGICAL ANALYSIS OF SOILS¹

By WILLIAM H. FRY
Received August 17, 1912

Soil may be considered as a mixture of solid, liquid and gaseous matter. The solid matter consists of mineral and organic material which react with

¹ Published by permission of the Secretary of Agriculture.

each other and with the liquid and gaseous material. By far the larger part of the solids, the débris of rocks, is a mixture of minerals. These minerals comprising the greater part of the soil furnish part of the so-called plant food to vegetation through the medium of the soil solution and is the chief factor influencing the texture of the soil. Much chemical work has been done upon the soil; but experience has shown that chemical analyses throw very little light upon many soil problems. So far, very little work of a purely mineralogical character has been done in connection with these problems, especially in America. This is rather surprising considering the importance of an accurate knowledge of all soil constituents and the recent high development of petrographic methods. Work has been undertaken by the Bureau of Soils which, it is hoped, will put the subject of soil mineralogy upon a firm basis and create interest in a subject which cannot fail to be of great value to both the farmer and the scientist engaged with agricultural problems.

Certain generalizations concerning the component soil minerals have been established. Thus, chemical analyses have proven that the larger part of the potash and phosphatic material is concentrated in the finer mechanical separates of the soil.¹ The most far-reaching and important generalization yet reached is that "practically every soil contains all the common rock-forming minerals."²

Of course the relative proportions of soil minerals may and do vary widely. But the number of minerals that can be found in even an apparently pure quartzose beach sand is often quite large. The extreme mineralogical heterogeneity of soils is not surprising, when their origin and the various processes, both physical and chemical, to which they are subjected are considered. All rocks, while they may consist essentially of only a few minerals, do, in reality, contain a large number of species when sufficiently large masses of the rock are considered. In the processes of weathering, the rarer mineral species are concentrated. The various weathering processes alter certain minerals, thus giving rise to other species. Wind and water, by their transporting and mixing action, add many minerals to soils.³ Thus the mineral heterogeneity of soils is being constantly maintained.

In order to make a mineralogical analysis of a soil, certain preliminaries are often necessary and always advisable. Quartz constitutes by far the predominant part of practically all soils and it is often convenient to eliminate this mineral from the sample in order to decrease the time which would otherwise be consumed in locating the various minerals to be determined. This elimination can be easily accomplished by means

of heavy solutions, such as methylene iodide or Thoutlet's solution in connection with an Harada separator or other specially constructed tubes. Minerals containing magnetic elements, as iron, can be eliminated by means of an electro-magnet. The portions from these separations will be found to lend themselves much more readily to a rapid mineralogical analysis than do the unseparated soils. In order to separate the component minerals according to size of grain, a series of sieves supplemented by the method of centrifugal mechanical analysis⁴ is used. By this method the soil is separated into various portions, the diameters of the grains of each portion being constant within quite narrow limits. This separation according to size is necessary when quantitative results are required. Various microchemical tests may be used in the determination of many of the minerals, and direct chemical tests upon the soil will often aid in the detection of the presence or absence of certain groups of minerals, such, for example, as the sulfates or chlorides.

For the determination of the optical constants of the minerals, a petrographic microscope is desirable. But any microscope which can be adjusted with a condensing lens, nicol prisms, both analyzer and polarizer, a rotating stage, and an eye-piece with cross hairs, can be used.

After the material has been prepared for the examination, a small quantity is transferred to a microscopic slide. The material is then embedded in an oil of a definite refractive index. A series of oils with definite refractive indices are kept for this purpose. An oil having an index nearly equal to that of quartz serves best as a general embedding medium. The preparation is now covered with a cover glass and is ready for examination. The refractive index of any particular grain can be determined by comparison with the oil in which it is embedded. Should the indices of the mineral be either higher or lower than that of the oil, the grain will stand out with a noticeable relief. Whether the index of the grain is higher or lower can be determined by means of the Beche lines or by the method of inclined illumination of Schroeder van der Kolk.⁵ Various oils may be used until one is found with practically the same index of refraction as that of the mineral, or the index may be roughly approximated, after a little practice, by the relief of the mineral.

The index of refraction having been determined, or approximated, the other optical characteristics are determined. By crossing the nicols and rotating the stage, it is immediately determined whether the mineral is isotropic or anisotropic, except in cases of a uniaxial mineral perpendicular to an optic axis, in which case an interference figure can be obtained, since isotropic minerals remain dark during the rota-

¹ G. H. Failyer, J. G. Smith and H. R. Wade, "The Mineral Composition of Soil Particles," *Bull.* **64**, Bureau of Soils, U. S. Department of Agriculture.

² F. K. Cameron and J. M. Bell, "Mineral Constituents of the Soil Solution," *Bull.* **30**, Bureau of Soils, U. S. Department of Agriculture; F. K. Cameron, "The Soil Solution" (1911); "An Introduction to the Study of the Soil Solution," *Jour. Phys. Chem.*, **14**, 320-451 (1910).

³ E. E. Free, "The Movement of Soil Material by the Wind, with a Bibliography of Eolian Geology," by S. C. Stuntz and E. E. Free, *Bull.* **68**, Bureau of Soils, U. S. Department of Agriculture (1910).

⁴ Lyman J. Briggs, F. O. Martin and J. K. Pearce, "The Centrifugal Method of Mechanical Soil Analysis," *Bull.* **24**, Bureau of Soils, U. S. Department of Agriculture.

⁵ A detailed account of all methods used in microscopic soil mineralogy will be found in a forthcoming bulletin of this Bureau. "The Microscopic Determination of Soil-forming Minerals," by W. J. McCaughey and W. H. Fry.

tion. Should the mineral be anisotropic, whether it is uniaxial or biaxial, is determined by means of interference figures obtained by crossing the nicols and removing the eye-piece. Uniaxial minerals give a dark cross, biaxial mineral either one or two hyperbolae according to the optical orientation of the grain. The extinction angle can be measured by aligning a cleavage crack or crystal face of the grain with one of the cross hairs and rotating the stage until the grain becomes dark. The position or negative character of the mineral is obtained with the aid of a quartz or mica wedge or selenite plate. These characters in conjunction with the refractive index and the morphological character of the mineral, cleavage, form, and so forth, are usually sufficient to identify the mineral. Should they not be sufficient, then further optical tests may be applied, such as the measurement of the optic angle, and so on. All of these tests can be performed very quickly. Then another mineral grain in the preparation is selected and the same procedure applied to it, until all of the grains in the preparation have been determined.

Should quantitative results be desired, they are obtained by the aid of an eye-piece checkerwork micrometer. The minerals in the preparation being known, and all being of practically the same diameter, the percentage of any one or more species of the mineral can be gotten by count in conjunction with the micrometer as an aid and check.

So far, the limitations of the microscope have prevented the examination of the mechanical separates other than the sands and the silts. The clays, on account of the extreme minuteness of the grains, do not lend themselves to a microscopic mineralogical analysis.

A large number of analyses have been made by this laboratory and will be published in other connections where they will be fully discussed. A few only, taken more or less at random, are given here, to give some idea of the mineral complexity of the soil. Only one quantitative examination is included.

SOIL SERIES, CECIL, W. J. McCAUGHEY (ANALYST)

Minerals other than quartz	
SAND	SILT
3-5 per cent.	10 per cent.
Abundant and characteristic mineral	
Zircon	Sillimanite
Sillimanite	Chlorite
Rutile	Muscovite
Microcline	Orthoclase
Plagioclase	
Biotite	
Less abundant or accessory minerals	
Epidote	Garnet
Muscovite	Hornblende
	Epidote
	Tourmaline

Remarks: Stretched and undulatory quartzes. Grain mostly sub-angular.

From this analysis it is seen that quartz constitutes by far the larger percentage of the separates examined. In all, fourteen minerals were determined.

Some qualitative analyses of various soils are as follows:

Sierra Sandy Loam from Sacramento Area.—Magnetite, quartz, anorthite, andesine, oligoclase, labradorite, orthoclase, microcline, hornblende, hypssthene, zoisite, muscovite, biotite, tourmaline, epidote, zircon.

Orangeburg Sandy Loam.—Magnetite, quartz, oligoclase, microcline, orthoclase, albite (oligoclase-albite), labradorite, biotite, garnet, zircon, epidote, apatite (enclosed in quartz), muscovite.

This soil seems very low in ferric minerals.

Norfolk Sandy Loam.—Quartz, apatite (enclosed in quartz), rutile (enclosed in quartz), tourmaline, magnetite, albite, hornblende, augite, topaz, biotite, andalusite, olivine.

It will be noticed that orthoclase does not appear in this analysis. However, the mineral has been located in small quantities of other samples of the same soil.

Sample Taken from Bed of Creek, Old Brunswick Cove.—Quartz, magnetite, andesine, labradorite, apatite, hornblende, biotite, muscovite, orthoclase.

These analyses represent the sands and silts. It is extremely probable that the clays contain all of the minerals found in the separates of the larger particles. Attrition would inevitably cause particles of the larger minerals to find their place in the clays. In addition, it is known that the clays contain large amounts of kaolin and ferruginous matter. Chemical analyses lead us to believe that the mineralogical composition of the clays is far more complex than that of the sands and silts. Work is now in progress which it is believed will demonstrate this.

The most immediate and obvious results of the mineralogical analysis of a soil is that the method gives a rapid qualitative analysis, far more rapid than the ordinary chemical methods. For instance, only a few moments are necessary to determine whether apatite is present abundantly or otherwise. By making a quantitative examination, an approximate idea can be formed as to the amount in the particular soil under examination. Further, the method shows definitely in what form the chemical elements are combined, a result which a chemical analysis leaves to conjecture or to probability. Something concerning the origin of the soil can be learned by the method. If, for example, a soil should contain large quantities of ferro-magnesian minerals, it undoubtedly was derived largely from some basic crystalline rock, which particular rock would of course depend on the mineral species present taken in conjunction with other predominant minerals of the soil. Results have already thrown some light on soil fertility and considerable on ground rock fertilizer problems.¹ It is possible that the method may be the means of constructing a mineralogical classification of soils.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

¹ See a forthcoming bulletin of this Bureau, "Ground Rock and Ground Minerals as Fertilizers," by W. O. Robinson and W. H. Fry.

THE SIGNIFICANCE OF THE LIME-MAGNESIA RATIO IN SOIL ANALYSES

By P. L. GILE AND C. N. AGEYON

Received Sept. 13, 1912

Some twelve years ago Loew announced the hypothesis that plants make their maximum growth, other factors of course being favorable, only when the available lime and magnesia are present in a certain ratio. All the details of this hypothesis do not require repetition here. Briefly, it is held that an excess of either lime or magnesia in the soil is injurious, and that by increasing the deficient element until a ratio of CaO to MgO of 1/1 to 4/1 obtains (the optimum ratio varying for different crops), a more favorable condition for growth is secured. Investigators in different countries have tested Loew's hypothesis in water and pot culture experiments. Without reviewing all these experiments,¹ the results in some cases have been confirmatory and in others contradictory.

It is evident that if this hypothesis holds true under soil conditions, the lime-magnesia ratio is of the utmost significance in soil analysis²—determining one of the

lends it plausibility, since there are so many physical, chemical, and biological factors involved in fertility.

LIME-MAGNESIA RATIO IN SOILS OF PORTO RICO

In a survey of the soils planted to pineapples³ it was found that the soils producing vigorous plants and good yields of fruit contained lime and magnesia in the following ratios: 1/5, 13/1, 3/1, 3/1, 6/1, 10/1, 25/1, 40/1, 73/1, 1/2, 27/1, 1/13, 7/1, 8/1, 7/1, 14/1, 12/1, 1/3.³ Four soils analyzed from the Florida Keys had the ratios of CaO/MgO of 38/1, 30/1, 100/1 and 500/1.

In some of the soils where the ratio is very wide there is less than 1 per cent. of CaO and only a trace of MgO. Where both the bases are present in such small quantities it might very well be that an unfavorable ratio would not affect the fertility to such an extent as though they were present in greater quantities. However, a particularly fertile soil, producing some of the finest pineapple plants on the Island and supporting a luxuriant citrus grove, contained 4.25 per cent. of CaO, 0.17 per cent. of MgO, and 0.24 per cent. of CO₂. The lime-magnesia ratio

TABLE I.—ANALYSES OF SOILS FROM HACIENDAS "MERCEDITA" AND "FLORIDA"

	Soil	Sub-soil	Soil	Sub-soil	Soil	Sub-soil	Soil	Sub-soil
Number of sample.....	391	392	400	401	422	423	452	453
Insoluble residue.....	33.89	32.56	28.39	19.53	23.73	21.45	24.81	9.48
Volatile matter.....	29.14	28.76	31.48	35.52	34.53	34.40	32.27	39.16
Alumina, Al ₂ O ₃	4.34	5.98	5.08	3.85	4.59	4.42	8.54	4.07
Iron, Fe ₂ O ₃	4.10	4.05	3.75	2.56	3.40	3.82	4.34	1.06
Lime, CaO.....	26.11	27.21	29.23	36.79	32.19	34.21	28.78	45.53
Magnesia, MgO.....	0.22	trace	trace	0.91	1.32	1.56	0.69	0.59
Potash, K ₂ O.....	0.57	0.63	0.16	0.25	0.05	0.04	0.42	0.33
Phosphoric acid, P ₂ O ₅	0.16	0.05	0.14	0.13	0.19	0.10	0.19	0.10
Total.....	98.53	99.24	98.23	99.54	100.00	100.00	100.04	100.32
Nitrogen, N.....	.22	.01	.20	.14	.33	.23	.09	.03
Carbon dioxide, CO ₂	19.72	20.20	21.69	27.91	26.81	24.85	21.99	35.70
Calcium carbonate, CaCO ₃	44.86	45.94	49.34	63.49	60.99	56.54	50.27	81.22
Reaction to litmus.....	alk.	alk.	alk.	alk.	alk.	alk.	alk.	alk.

fertility factors, and showing the need of an application of either lime or magnesia. Soil investigations carried on in Porto Rico during the last five years afford data that bear upon this subject. Also a series of experiments have been conducted which show that the lime-magnesia ratio affects the growth of plants under some conditions but not under others.

Analyses made of the typical soils planted to pineapples and sugar cane show that the content of lime and magnesia varies greatly. If the hypothesis of Loew holds true for soil conditions and the ratio of lime to magnesia is one of the controlling factors in fertility, then those soils with a very unfavorable ratio should be of low productivity. If the soils with unfavorable ratios are not of low productivity it would seem to show that the hypothesis is not tenable, at least not for all soil conditions. On the other hand, the fact that some soils with favorable ratios are fertile and other soils with unfavorable ratios are unfertile does not prove the hypothesis, but merely

in this soil, then, was 25/1 and the absolute quantity of lime was high.

The soils from the Florida Keys which have the lime-magnesia ratios of 38/1, 30/1, 100/1, and 500/1 contain, respectively, 21.13 per cent. CaO and 0.56 per cent. MgO, 20.34 per cent. CaO and 0.69 per cent. MgO, 17.01 per cent. CaO and 0.17 per cent. MgO, 10.96 per cent. CaO and trace of MgO. The analyses show that the lime is present partly as carbonate and partly combined with organic matter. These soils are reported as bearing a good crop of pineapples. They are exceptional in containing a tremendous amount of organic matter. Because of the high content of organic matter pineapples grow well in these soils although they will not succeed in ordinary soils containing 2 per cent. of carbonate of lime.³

These soil analyses show that the good pineapple soils of Porto Rico have, on an average, wide lime-magnesia ratios, that an *exceptionally* fertile soil has

¹ Bull. 11, P. R. Agr. Expt. Station.

² References to the different experiments are given in *Circ.* 10 and *Bull.* 12 of the P. R. Agr. Expt. Station.

³ For determining the lime and magnesia available to, or affecting the plants, Loew prescribes digestion of the fine earth with 10 per cent. hydrochloric acid—practically the method of the A. O. A. C.

² In some of the analyses reported in *Bull.* 11 the magnesia is present only as a trace. In calculating the ratios for these soils it is assumed that 0.02 per cent. of MgO is present, although the amount is probably nearer 0.01 per cent. or less.

³ P. L. Gile, *Bull.* 11, P. R. Agr. Expt. Station.

a ratio of 25/1, and that some soils having ratios of 30/1 to 500/1 are at least ordinarily productive.

A partial survey has also been made of the soils planted to sugar cane. Most of the clay lands carry from 0.2 per cent. to 1.50 per cent. of lime and from 0.5 per cent. to 2.00 per cent. of magnesia and no carbonate, most of the lime and magnesia probably being present as silicates, as the soils are low in organic matter. In these clay soils the ratio of lime to magnesia runs 1/1, 1/4, 4/5, 1/2, 2/5, 3/2, 1/3, 1/2, 1/3, 3/2, or generally with the magnesia slightly in excess of the lime. Some of these soils are quite productive and others very unproductive. There is no correlation between the fertility and the lime-magnesia ratio, as was to be expected.

Certain of the loamy soils, however, show great variations in the content of lime and magnesia. In Table I are given the acid analyses of four samples of surface soil with the sub-soil. Samples 391, 400, 422, and 452 represent the surface foot of soil, and samples 392, 401, 432, and 453 are the respective sub-soils taken from the first to second foot. Each sample is a composite of three borings.

Samples 391, 400 and 422 are all taken from different areas in a field belonging to Central "Mercedita" near Ponce, P. R. This field is planted to sugar cane and is one of the most productive cane soils on the Island. Last year the average return from this field for plant cane was over sixty tons of sugar cane (variety Cristalina) per acre. This is an exceptional yield for Porto Rico and a very good yield for any country.

Samples 452 and 453 are the soil and sub-soil respectively of a field in Hacienda, "Florida," Yauco, P. R. This field is on a rather steep side hill and, while it does not produce so much as the valleys below, it is, with irrigation, a fairly productive soil. The analysis would seem to show the crops were limited more by the nitrogen supply than anything else.

The above analyses show that in different parts of the "Mercedita" field the first foot of soil contains lime and magnesia in various ratios of 119/1, 1461/1 and 24/1 and the respective sub-soils have ratios of 1360/1, 40/1 and 22/1. In the "Florida" field the top soil contains lime and magnesia in the ratio of 42/1 and in the sub-soil the ratio is 77/1.

The areas where the different samples were taken were selected as representatively fertile areas. As each sample is a composite of three separated borings it is evident that the fields were fairly sampled. The determination of carbon dioxide in these soils shows that the lime, at least, is present as carbonate, thus in an easily available form.

The above analyses show that sugar cane can grow luxuriantly in soils containing a tremendous excess of lime over magnesia, providing the other fertility factors are in proper condition. It is, of course, not impossible that still larger crops might be obtained from the "Mercedita" field if the lime-magnesia ratio were nearer 1, but in view of the exceptional yield this is very improbable.

We are then confronted with the facts; that some

soils with lime-magnesia ratios of 30/1 to 500/1 are productive pineapple soils; that one soil with the ratio of 25/1 is an exceptionally productive soil for citrus fruits and pineapples; that another soil where the ratio varies from 22/1 to 1461/1 is an exceptionally productive soil for sugar cane. Thus the observations of Porto Rican soils would seem to show that in soil analyses the ratio of lime to magnesia is of no significance and that cases where the ratio parallels the fertility are due to chance. The many pot experiments of other investigators which have failed to show any influence of the lime-magnesia ratio¹ make it clear that the above observations are not exceptional.

CONDITIONS UNDER WHICH THE RATIO MAY INFLUENCE GROWTH

The above analyses do not show, however, that there is no physiological basis for Loew's hypothesis. In fact, from the work of Loew and numerous investigators it is apparent that under certain artificial conditions the ratio of lime to magnesia may markedly influence growth.

The results obtained by Osterhout,² Kearney and Cameron,³ Lipman,⁴ and Hansteen⁵ show that in certain solutions (containing few salts) not only the ratio of lime to magnesia affects growth, but also the ratio of other bases. From the work of the above investigators and also of Benecke,⁶ it is apparent that solutions of various single nutritive salts are toxic to plant and lower animal life. A mixture of two salts is less toxic than either alone and, in a more complex mixture, all the salts which are toxic alone may lose their toxicity. Lime salts exert the strongest antagonism in overcoming the toxicity of magnesium salts although lime is not specific in this antagonism. These facts furnish a physiological basis for such an hypothesis as that of Loew. The hypothesis of the lime-magnesia ratio, however, does not explain the generality of these facts but merely the special case of the antagonism between lime and magnesia.

This work on the antagonism of various salts in solution does not necessarily show that the ratio of lime to magnesia affects growth under all conditions. In a series of experiments made by one of us,⁷ where rice was grown in a complete nutrient solution containing lime and magnesia in excess, it was found that the concentration influenced the effect produced by the ratio of lime to magnesia. When the lime and magnesia were present in concentrated solutions, the ratio of these bases markedly influenced the growth. As the concentration of the lime and magnesia was diminished, however, the influence of the ratio diminished. In dilute solutions, ratios of lime to magnesia between 10/1 and 1/10 had no effect on the growth.

This work mentioned above, on the toxicity of va-

¹ D. Meyer, *Landw. Jahrb.*, **1904**, p. 371. D. Meyer, *Landw. Jahrb.*, **1910**, *Ergänzungsband III*, p. 254. O. Lemmermann, et al., *Landw. Jahrb.*, **40**, Nos. 1-2.

² W. J. V. Osterhout, *Bot. Gaz.*, **44**, 259.

³ Kearney and Cameron, U. S. Dept. Agr., *Report 71* (1902).

⁴ Chas. B. Lipman, *Bot. Gaz.*, **48**, 105.

⁵ B. Hansteen, *Jahrb. f. wiss. Botanik*, **47**, 289.

⁶ W. Benecke, *Ber. d. D. Bot. Gesell.*, **25**, 322.

⁷ P. L. Gile, *Bull.* **13**, P. R. Agr. Expt. Sta.

rious single salts and the antagonistic action of other salts in overcoming the toxicity, applies to conditions obtaining in solutions. Because the addition of lime exerts a strong antagonism in overcoming the toxicity of a solution of magnesia and *vice versa*, it does not necessarily follow that such an antagonistic action is exerted in ordinary soils. In ordinary soils it is probable that the ratio of the bases has no bearing on the fertility in the respect noted above, for the following reasons:

1. The soil particles exert a physical effect in diminishing the toxicity of any salt solution. Jensen found that in quartz sand much higher concentrations of toxic salts were required to produce death than in water cultures.¹

2. The soil solution is a more or less balanced solution, containing a great variety of ions, and undissociated molecules.²

3. The soil solution, so far as we can determine, is a dilute solution.

These acts, of course, do not apply to soils impregnated with alkali salts. In alkali soils we might expect to find the productivity influenced by the ratio of lime to magnesia, as well as by the ratios of other bases,³ since in such soils we have relatively concentrated solutions of soluble salts.

The experiments with soils in pot cultures to test the hypothesis have thus far given conflicting results. The method of these experiments has been to add the carbonates, sulphates, and chlorides of lime and magnesia to different soils to alter the lime-magnesia ratios. The pot experiments of Loew and his co-workers in Japan have apparently confirmed the theory.⁴ These experiments have been criticized on the ground that they were not always carried out in duplicate, that too few plants were grown, and that the conclusions were not always based on the relative weights of the plants but sometimes on the relative heights and number of branches.⁵ The pot experiments of Meyer⁶ and of Lemmermann, Einecke and Fischer,⁷ which are by far the most exhaustive on the subject, have given negative results. These have been criticized on the ground that too many plants were grown per pot and that insufficient fertilizer was supplied.⁸

It should be borne in mind in judging these experiments that when large doses of the carbonates or oxides of lime and magnesia are added to the soil, not only the ratio of lime to magnesia is altered, but also the reaction of the soil. Since ground marble, ground magnesite, precipitated calcium carbonate and precipitated magnesium carbonate vary in the intensity

of their action,⁹ a mixture of ground marble and ground magnesite will induce a reaction different from that induced by either alone. It has been amply shown that the reaction of a soil is one of the strongest factors in determining the growth of certain plants. Hence in the experiments where large amounts of lime and magnesium carbonates were applied to the soil the results in many cases may be attributed as well to variations in the soil reaction as to variations in the lime-magnesia ratio.

SUMMARY

The soil experiments to test directly the effect of the lime-magnesia ratio on the growth of plants have given conflicting results. This lack of agreement may be due to the fact that some of the experiments were not properly carried out; or it may be that the apparently confirmatory results arrived at by some investigators are to be attributed rather to alterations in the soil reaction than to the lime-magnesia ratio. From the effect of salts on plants grown in water cultures we should not expect plants to be influenced by the ratio of the bases under the conditions obtaining in any but alkali soils. From field observations it is certain that soils with an exceedingly wide ratio of lime to magnesia may be exceptionally fertile. Hence it would appear that in analyses of ordinary soils the ratio of lime to magnesia is of no significance, but in analyses of the soluble salts of alkali soils the ratio of lime to magnesia may be exceedingly important.

PORTO RICO AGRICULTURAL EXPERIMENT STATION
MAYAGUEZ

A PROPOSED MODIFICATION OF THE OFFICIAL METHOD OF DETERMINING HUMUS

By O. C. SMITH

Received August 24, 1912

The determination of the humus content of soils has always presented difficulties because of the inability to obtain a clear solution for evaporation. There have been several methods proposed but none of them have given very good satisfaction on all soils. By adding ammonium carbonate solution, a clear filtrate is obtained. By evaporating to dryness and again extracting with 4 per cent. ammonium hydroxide a clear solution is obtained, but this process is long and tedious and some of the humus is apt to be occluded by the precipitate of clay. Other methods for obtaining clear solutions are by the use of a Pasteur filter, a centrifuge and a modified clay filter.

The official method states that the 4 per cent. ammonium hydroxide solution should be shaken for the first twenty-four hours and then allowed to stand twelve hours and settle. The clearest part is then drawn off, filtered, and the determination made without any further treatment. This filtering does practically no good, and it is only very rarely that enough clear solution can be obtained in this way to make the determination satisfactorily. Our experience shows, however, that if the sediment is not allowed to settle, but is shaken well, and all of the soil possible is poured

¹ S. H. Jensen, *Bot. Gaz.*, **43**, 11.

² How successive additions of various ions diminish the toxicity of a solution is shown by W. J. V. Osterhout, *Bot. Gaz.*, **44**, 259.

³ Kearney and Cameron, *Loc. cit.*

⁴ Vd. Reports in Vol. I, Nos. 1 and 2, of Agr. Expt. Sta., Tokyo; also Vols. IV., V., VI., VII., of Col. of Agr., Tokyo Imp. Univ.

⁵ O. Lemmermann, et al., *Landw. Jahrb.*, **11**, Nos. 1-2, p. 177.

⁶ D. Meyer, *Landw. Jahrb.*, **1904**, 371; **39**, 254 (1910) (Enganzungs-band III).

⁷ O. Lemmermann, A. Einecke, H. Fischer, *Landw. Jahrb.*, **40**, Nos. 1-2.

⁸ Loew, *Ibid.*, **42**, 181 (1912).

⁹ D. Meyer, *Landw. Jahrb.*, **1904**, 371; also Kossovich and Althausen, *Exp. Sta. Record*, **23**, 226.

onto the filter, a perfectly clear solution can easily be obtained. At first the filtrate is as turbid as that in the funnel. This may be returned to the filter or discarded; but after about five or six hours, the filtrate in most cases is clear. With soils running high in humus percentages, a clear filtrate can often be obtained in an hour or two; while in clay, especially red clay soils, it may be twelve hours before the solution runs clear. But a clear solution is always obtained. In determining the humus in over 200 soils, there was not one that did not give a perfectly clear filtrate and only one or two that took more than twelve hours. If the filtering is started in the morning, by night the filtrate is clear in most cases, and the next morning two or three hundred cc. will have filtered through perfectly clear.

After the first two or three hundred cc. have run through, the filtering is generally very slow and to prevent losses by evaporation the funnels are placed directly into Erlenmeyer flasks and covered by watch glasses. It has been found best to use five- or six-inch funnels and Schleicher and Schüll folded filters with hardened points, twenty-four or thirty cm. in diameter. With this size enough solution can be poured in at once to run for four or five hours. Generally one filter full is all that is needed to start a clear filtrate, but until this is obtained the filter should be kept nearly full so as to deposit a layer of soil over the entire paper.

Several different papers and combinations of papers have been tried. On one set, S. & S. hardened was used for one of the duplicates and the ordinary S. & S. folded with hardened points for the other; using both of these on the same funnel was also tried; cheap papers did not give as good results although a clear solution was obtained. The double papers or the hardened did not give a clear filtrate any sooner than the folded and the filtration was much slower. Any first-class paper is all right if it is strong enough to hold the three to five hundred cc. of solution that is put on it. By using this method of obtaining a clear filtrate it is very seldom that the duplicates do not check to within one-tenth of one per cent.

Below is a fair sample of the results obtained:

Weight of soil used, 10 grams: aliquot taken, one-fifth

Lab. No.	Dish and humus dry Grams	Dish after ignition Grams	Loss on ignition Gram	Humus Per cent.
108-5-23	47.1325	47.1186	0.0139	0.70
	49.0290	49.0165	0.0125	0.63
108-5-25	49.0508	49.0431	0.0077	0.39
	48.0067	47.9987	0.0080	0.40
108-5-27	38.9278	38.9163	0.0115	0.58
	39.5477	39.5358	0.0119	0.60
108-5-30	50.3218	50.3036	0.0182	0.91
	49.0553	49.0378	0.0175	0.88
108-5-36	49.5910	49.5615	0.0295	1.48
	48.9532	48.9253	0.0279	1.40
108-5-55	48.3436	48.3012	0.0425	2.13
	47.3165	47.2732	0.0433	2.17

A comparison of this method was made with the Mooers and Hampton method and the Rather method. The last two methods were run at a previous time by Chemist No. 1 of this laboratory. In his work a lower result was obtained for the Rather method in nearly

every case. The author took the same soils and determined the humus by the Rather and simple filtration methods. Chemist No. 3, also of this laboratory, determined the humus by the latter only.

The solutions were prepared according to the Official method by washing with one per cent. hydrochloric acid and water and digesting with four per cent. ammonium hydroxide for twenty-four hours. At the end of the digestion, a filter full was taken from the flask and the remainder set aside to stand twelve hours and settle for the Rather method. At the end of this time, 130 cc. of the solution were decanted through a filter and 0.650 gram of ammonium carbonate was added and shaken when dissolved. This solution was again allowed to stand twelve hours and settle, when it was again decanted through a filter, 100 cc. were evaporated, dried five hours at 100°, weighed, ignited and again weighed. This took forty-eight hours from the time the four per cent. ammonium hydroxide was added until the solution was ready for evaporation.

With the Smith method, the filtering was started as soon as the soil had digested twenty-four hours. Three hours afterwards, the filtrate was clear and at the end of twelve hours, 200 cc. of clear solution had run through. From this, 100 cc. were drawn and the drying and ignition made exactly as in the Rather method. By this method it was thirty-six hours from the time ammonium hydroxide was added until the solution was ready for evaporation, thus gaining twelve hours: 130 cc. of the clear filtrate by the latter method were taken immediately after drawing the sample for the analysis and 0.650 gram of ammonium carbonate was added. These solutions were treated exactly as the Rather method solutions were and at the end of twenty-four hours there was no sign of a precipitate, in any case. All of the filtrates were compared as to color and in every case the solution obtained by simple filtration was richer in color than that obtained by the Rather method. This color was evidently taken from the solution in the Rather method by the action of the ammonium carbonate, or by the heavy flocculent precipitate. However, the ammonium carbonate did not have any effect on this color when the solution was obtained clear by simple filtration.

COMPARISON OF METHODS FOR THE DETERMINATION OF HUMUS

Lab. No.	Mooers-Hampton method Chemist		Rather method No. 1		Rather method Chemist		Smith method No. 2		Smith method Chemist No. 3	
	%	%	%	%	%	%	%	%	%	%
12-1-110	1.478	1.14	1.175	0.38	1.545	0.228	1.498	0.448	1.568	2.16
12-1-111	0.700	0.64	0.470	0.34	0.560	0.230	0.693	0.490	0.773	1.278
12-1-115	0.660	0.54	0.343	0.26	0.558	0.208	0.708	0.750	0.773	1.358
12-1-117	0.523	..	0.310	..	0.478	0.158	0.440	0.478	0.528	1.073
12-1-120	1.275	..	1.063	..	1.348	0.218	1.363	0.700	1.485	2.340
12-1-122	1.093	..	0.775	..	0.933	0.168	0.845	0.585	0.988	1.580
12-1-123	0.458	..	0.325	..	0.408	0.200	0.438	0.665	0.528	1.470
12-1-142	1.740	..	1.498	..	1.705	0.300	1.803	0.793	1.880	2.620
12-1-143	1.073	..	0.895	..	0.898	0.160	0.980	0.918	1.030	1.770
Average	1.000	..	0.761	..	0.937	..	0.974	..	1.061	...

It will be observed from the above table that in every case the percentage of ash is larger in the Smith method than in the Rather method (both run by Chemist No. 2) but the percentage of humus is

nearly the same, the greatest difference being 0.15 per cent. in 12-1-115. It will also be seen that there is a variation in the results of the two different men using the same soils and Rather method, being a difference of 0.37 per cent. in soil 12-1-110. In only one soil, 12-1-143, do the results agree. This seems to indicate that if the exact amount of ammonium carbonate is not added each time and the solutions do not have exactly the same treatment, different results are obtained.

The per cent. of humus obtained by Chemist No. 3 was slightly higher than that obtained by Chemist No. 2; also the per cent. of ash was higher. But this is easily explained by the fact that this determination was the first time Chemist No. 3 had used this method. The solutions from which he drew his aliquot gave a slight deposit of clay on standing. He did not allow the filtrate to become perfectly clear before he took the portion for the determination. In our routine analyses, we allowed about fifty of these solutions to stand two weeks and at the end of that time only two or three showed any precipitate at all. The greatest difference between the results of the two men doing the proposed method is 0.14 per cent. in soil 12-1-122, notwithstanding the fact that one of the men had never used the method before.

SUMMARY

1. The weighing out of an exact amount of ammonium carbonate is not necessary.
2. The time taken for the determination is shorter in most cases.
3. Nothing is added that could precipitate part of the humus.
4. It seems to give more uniform results.

DEPARTMENT OF AGRICULTURAL CHEMISTRY
UNIVERSITY OF MISSOURI
COLUMBIA

THE DETERMINATION OF LIME IN COW FECES¹

By R. ADAMS DUTCHER

Received June 8, 1912

While conducting the analytical work on the ash of cow feces, in a mineral nutrition experiment, it was found that the results were not concordant. This is due to the fact that the ash of cow feces runs abnormally high. The ash content of the feces used in this investigation was 20.55 per cent., while Dr. P. F. Trowbridge,² of the Missouri Experiment Station, has found the ash to run as high as 39 per cent. This unusually high ash content is due to the large amount of sand, dirt, etc., that the cow receives with the feed.

Methods of ash analysis are very lax with reference to the acid treatment of the ash. The time varies from 10 minutes³ boiling with acid, for plant ash; to 10 hours⁴ digestion over steam, for soils.

As nothing could be found relating to the ash of cow feces, it was decided to determine the factors which influenced the removal of the mineral constituents.

¹ Abstract of thesis submitted in partial fulfillment for Degree of Master of Arts, University of Missouri, 1912.

² Private communication.

³ "Food Inspection and Analysis," Leach, p. 303.

⁴ *Bulletin 107*, Official and Provisional Methods, U. S. Dept. of Agriculture.

The preliminary work showed that the calcium was the constituent removed with the greatest difficulty and therefore might serve as an index to all of the other mineral constituents.

The factors which it seemed necessary to determine may be outlined as follows:—

1. The time necessary to remove the lime by, (a) digestion of ash with acid over steam, (b) boiling the ash with acid on a hot plate.
2. The comparison of the efficiency of dilute and concentrated acid. (It was finally concluded to use concentrated hydrochloric acid, concentrated nitric acid and dilute hydrochloric acid of specific gravity 1.11.¹ This dilution is made by mixing equal parts of concentrated hydrochloric acid and water.)
3. The determination of which acid (nitric or hydrochloric) is most efficient.
4. The effect of dilute sodium hydroxide to break up silicates not decomposed by acid.
5. The efficiency of moist combustion as compared with ordinary combustion.

The feces were ground to a fine powder when dry and preserved in air-tight bottles. A large portion of the powdered sample was ashed to a cream white ash and preserved for analysis.

The moist combustions were conducted in Kjeldahl flasks, the boiling of the ash was conducted in Erlenmeyer flasks and the digestions were made in beakers, all of which were made of standard glass. Watch glass covers (on the beakers) and test tubes of water (suspended in the flasks) acted as condensers, and prevented loss of acid by evaporation.

After treatment with acid, the sample was diluted to twice its volume to prevent the acid from attacking the filter paper, and the sample was filtered and washed. The filtrate was then evaporated to dryness. The silica residue was taken up with dilute acid, filtered and washed. This filtrate was made up to volume for analysis.

Aliquots were made alkaline with ammonium hydroxide and brought back to faint acidity with acetic acid. After boiling a few seconds, the insoluble phosphates were filtered off and washed thoroughly.

The calcium was then precipitated as the oxalate and determined with N/50 potassium permanganate in the usual manner.

The following data shows (1) that the lime is removed in a shorter period of time when the ash is boiled with acid than when it is digested over steam. (2) That the ash must be boiled three hours to insure complete removal of the lime. (3) That in digestion, concentrated acid is more efficient than the acid diluted 1:1. (4) That when boiled, the concentrated acid has no advantages over the weaker acid.

When the acid is incapable of breaking up the silicates, it is advisable to treat the large silica residue with sodium hydroxide as proposed by the Fresenius-Will method.² When these alkaline washings are

¹ This is the strength of acid used in soil analysis (*Bull. 107*, U. S. Dept. of Agriculture).

² *Jour. f. Gasbeleuchtung*, 49, 853 (1906).

TABLE I.—BOILING ON HOT PLATE

HCl (conc.)		HCl (1 : 1)	
Time	CaO Per cent	Time	CaO Per cent
10 minutes.....	1.36	5 minutes.....	1.34
30 ".....	1.40	10 ".....	1.34
1 hour.....	1.40	20 ".....	1.39
2 hours.....	1.44	30 ".....	1.37
3 ".....	1.48	40 ".....	1.39
4 ".....	1.47	1 hour.....	1.44
		2 hours.....	1.47
		3 ".....	1.46

TABLE II.—DIGESTION OVER STEAM

HCl (conc.)		HCl (1 : 1)	
Time	CaO Per cent.	Time	CaO Per cent.
1 hour.....	1.44	0.5 hour.....	1.33
5 hours.....	1.46	1 ".....	1.33
8 ".....	1.46	2 hours.....	1.37
10 ".....	1.47	3 ".....	1.37
		4 ".....	1.37
		5 ".....	1.38
		6 ".....	1.37
		10 ".....	1.47
		15 ".....	1.47

added to the acid solution, there is a distinct tendency toward higher results, as is shown by the fact that the writer obtained 1.50 per cent. of CaO when the alkali was used with the ash that had been treated with concentrated hydrochloric acid; and when the alkali

was used with the ash which had been treated with nitric acid, the per cent. of CaO was 1.49.

When the feces were destroyed with moist combustion by the use of concentrated nitric acid, the per cent. of CaO in the feces (not the ash) was 0.304; and when the feces were destroyed with aqua regia, the per cent. was 0.300.

If these percentages are divided by 0.2055 (the percentage of ash in the feces) we find the percentages of CaO in the ash to be 1.47 and 1.45, respectively. This seems to show that there are no insoluble compounds formed in the heat of ashing.

Where the feces were destroyed with moist combustion and the acid-insoluble residue was treated with dilute alkali, the per cent. of CaO was 0.314, which, divided by 0.2055 gives 1.52 per cent. There is, unquestionably, a slight tendency toward higher results when the alkali is used.

In conducting mineral analyses on the ash of cow feces the writer advises that the ash be boiled at least three hours with concentrated nitric or hydrochloric acid and that the acid-insoluble residue be evaporated to dryness with dilute sodium hydroxide to break up all silicates. This alkaline residue should then be taken up with dilute acid and added to the original solution for analysis.

UNIVERSITY OF MISSOURI
COLUMBIA

LABORATORY AND PLANT

THE PLANT OF THE SAKAI CELLULOID COMPANY AT SAKAI, JAPAN

By F. C. AXTELL

Received November 4, 1912

In the year 1908, the writer received a commission from the Mitsui family of Japan for the design and construction of a plant for the manufacture of celluloid in that country. A long previous experience in this and allied industries in the United States had demonstrated that the machinery and processes hitherto employed left much to be desired in the way of improvement, of which there had been practically none during twenty years. This condition was and is due, in all probability, to the mistaken policy of manufacturers in the maintenance of secrecy, as a consequence of which inventors, manufacturers of machinery and scientists are kept in ignorance of the necessity for the application of their knowledge and energies in the progressive improvement which is necessary to the proper development of any industry.

With these facts in view, the writer advised that he be permitted to design all machinery, have it constructed in the United States, design all buildings and send the architectural drawings to Japan, where work on the buildings might be prosecuted while the machinery and other apparatus were under construction in America. This proposal received the approval of the interested parties, and work was at once commenced. A corps of draftsmen and tracers was engaged, and as rapidly as detailed drawings of a

machine were finished, such drawings, together with the necessary specifications, were submitted to manufacturers for bids, contracts were drawn, the machinery constructed, tested and shipped to Japan. In the meantime, detailed drawings of all buildings had been prepared and sent forward and construction commenced.

For the erection of the plant, the Company had purchased a plot of ground containing about 15,000 tsubo (13 acres) situated on the Yamato river, at the northern limit of the old town of Sakai, and exactly five miles from the Imperial city of Osaka. Considerable difficulty was experienced in securing a site, by reason of the strict regulations relating to the contamination of streams by factory or other waste-matter—not for sanitary reasons, but for the protection of fish, which form an important item of the national diet. The advantages of the site selected were: (1) cheap transportation by canal directly to Sakai harbor on the Inland Sea; (2) a plentiful supply of unskilled labor; (3) good and unrestricted drainage; (4) its proximity to Osaka, which is the principal commercial and manufacturing city of Japan; and (5) the fact that a practically unlimited supply of ground water of excellent quality could be obtained. The disadvantages were: (1) that the ground was low, thus necessitating an enormous amount of filling, and (2) the fact that the plot had as its easterly boundary the twenty-foot embankment of the Nankai Railway, the only entrance to the plant from the main highway being by means of a

culvert, only eight feet in width, cut through this embankment.

In buildings devoted solely to the manufacture of celluloid (with one exception) the use of structures more than one story in height is not advisable; and as, in the design adopted, dry basements were required, the foundations were laid practically upon the surface of the ground; for, as the normal level of the water-table was but a few inches below the surface, excavation to any considerable depth, except at great expense, was impracticable. All buildings are of slow-burning mill construction, the concrete foundations are unusually massive, supported upon piling, and the walls are one and one-half and two brick in thick-

ness, only eight feet in width, cut through this embankment. river by hand and carried to the compound in small, shallow baskets attached to shoulder-poles borne by coolies. As the area to be filled measured something over seven and one-third acres and the height twelve feet, about one hundred and forty thousand cubic yards of sand were required; and this operation consumed the better part of a year. In the meantime machinery and interior fittings were installed, and when the sand filling was completed, outside pipelines were laid, steam and electric transmission structure erected, wide sidewalks connecting the ground-floors of all buildings at a uniform level were built, electric wiring and inside piping completed and the plant was ready for operation.

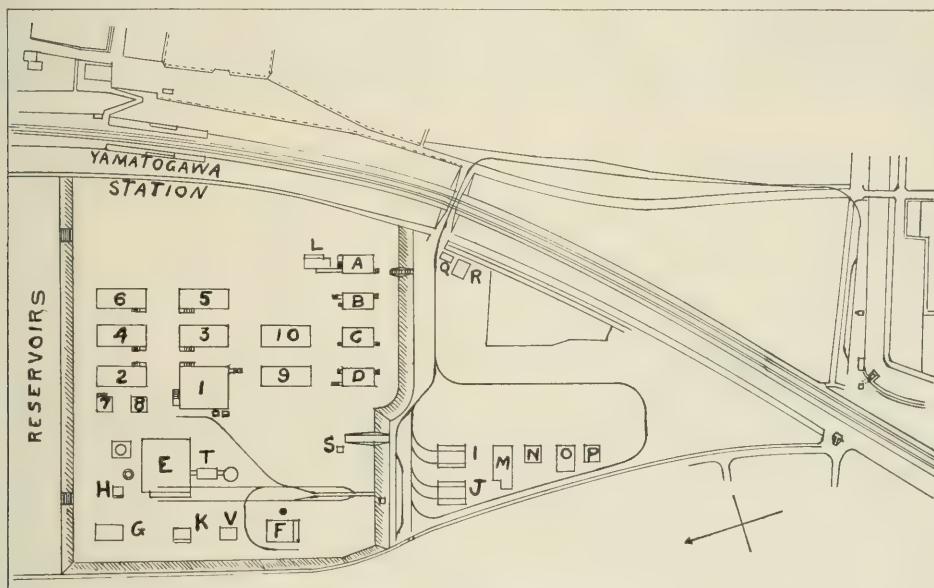


FIG. 1.—GENERAL PLAN OF SAKAI CELLULOID PLANT

- 1: Nitrating, washing and pulping.
- 2: Mixing, caking and pressing.
- 3: Welding, sheeting and the manufacture of tubes and rods.
- 4: Digesting and masticating.
- 5: Finishing.
- 6: Stock and shipping.
- 7: Granulating.
- 8: Crushing scrap material.
- 9 and 10: Seasoners.

- A: Office.
- B: Pipe, machine and carpenter shop.
- C: Designing and colormixing.
- D: Laboratory.
- E: Power-house.
- F: Nitric acid plant.
- G: Ice-making plant.
- H: Pump house.
- I and J: Storehouses.

- K and L: Toilets.
- M: Refractory.
- N, O and P: Storehouses.
- Q: Gate-keeper's lodge
- R: Wardrobe.
- S: Time-keeper's office
- T: Economizer.
- V: Blacksmith's shop.

ness, all brick being laid in a mixture of one part of Portland cement and three of sand. This very solid construction is due to the necessity for guarding against the effects of earthquakes, which are of frequent occurrence. Since the buildings were finished, a considerable number of shocks have been experienced, one of which, occurring August 14, 1909, was of great severity and destroyed a town some fifty miles from Sakai, but a subsequent careful examination of the buildings failed to show that they had been effected. All roofs are slated.

After the buildings were erected, filling of the compound was commenced. The filling-material consisted of coarse sand scooped from the bed of the Yamato

Fig. 1 is a general plan of the plant, showing the location of all buildings. As will be noted, the arrangement adopted is of the rectangular order, the buildings being separated by "avenues" and "streets," the clear space between buildings on the avenues being fifty feet and on the streets twenty-five feet. This arrangement results in very finely lighted and ventilated work-rooms and offers every facility for fire protection. In Fig. 1, the buildings devoted directly to the manufacture of celluloid are numbered 1 to 10, while those denoted by letter are used for the various purposes described.

WATER-SUPPLY

In the manufacture of celluloid the question of water



FIG. II—GENERAL VIEW FROM THE SOUTH



FIG. III—GENERAL VIEW FROM THE NORTHEAST, SHOWING WATER STORAGE RESERVOIRS



FIG. IV—NITRATING, WASHING AND SEASONING HOUSES

supply, both as regards quantity and quality, is one of great importance. For if the water used for washing the cellulose nitrate contains a large proportion of fixed solids, the transparency of the resultant product is affected; and if iron, manganese or certain forms of organic matter be present, a very objectionable yellow tinge is imparted, and attempts to correct these defects by boiling or bleaching the nitrate result, ultimately, in a diminution of the stability of the product. Hence, before purchasing the land, analyses of the water were made and submitted to the writer who pronounced it to be satisfactory. The water contains, normally, a trifle less than two hundred parts of total solids per million and the merest trace of iron.

As has been stated, the level of the water-table is but a few inches below the surface of the ground; and in order to insure a supply sufficient in quantity to meet emergencies, two reservoirs, each one hundred feet in length by twenty feet in width and twelve feet in depth, were excavated (see Figs. I and III). The walls of the excavations were lined with blocks of granite of a pyramidal shape, the bases of the pyramid forming the interior faces of the walls of the reservoirs, the apexes being turned outward and embedded in gravel, no cement whatever being used. Retaining-walls constructed in this manner have been found to be practically unaffected by seismic disturbances and in Japan there are numbers of such walls, built centuries ago, still in perfect condition.

The beds of the reservoirs were covered with six inches of fine and six inches of coarse gravel, and were connected by means of a lateral line of heavy stone-were pipe, eighteen inches in diameter, laid in concrete, a branch from this line, having the same dimensions and of similar construction, leading to the suction-well which is situated close to the north wall of the power-house. This well consists of a concrete shaft ten feet in diameter and about twenty-six feet in depth, and the suction-pipes from all pumps enter it at a height of about seven feet above the surface of the water, the foot-valves being immersed about ten feet below the same.

For the general water-supply, a steel water-tower with hemispherical bottom was provided, and is the first and only tower of this type thus far erected in Japan. By reason of the danger from earthquakes and the severe typhoons which occur, the high factor of safety of six was adopted in its design. At the time of the earthquake of August, 1909, a gang of riveters was at work in the tank at a height of one hundred and twenty feet, and they stated that the sway of the tank was about three feet from east to west. And later, during the same year, while the tank was still empty, a severe typhoon occurred, during which the wind attained a velocity of over eighty miles per hour; but no bad effects as a result of either of these disturbances could be detected. It is mentioned as being interesting, in that it is a practical demonstration of the stability of the modern steel water-tower.

The tank has a capacity of thirty-five thousand gallons and is supplied by an 8 × 10 inch triplex

pump, with direct motor drive and automatic control. The stand-pipe and all water-mains are of galvanized wrought iron, the mains being eight and six inches in diameter and the service-pipe to each building, except No. 1 and "E," four inches; in these it is six inches. Numerous gate-valves by means of which any section of the mains or laterals may be cut off for repairs, are provided and there is, of course, a cut-off valve in each service-pipe.

That portion of the water-supply which is used for washing the cellulose nitrate is passed through two large pressure-filters, filled with quartz sand, for the removal of any suspended matter.

Located at various points about the plant are hose-boxes of the type shown between the refectory and one of the storehouses in Fig. VII. The hydrants are located immediately in the rear of each of these boxes and the hose, of which each box contains one hundred feet of 2⁵/₈ inches with 1¹/₈ inch nozzle, is always connected thereto. These boxes are so located that at least two streams can be brought to bear upon any building, and on some buildings, such as Buildings 9 and 10, three or four streams are available. All buildings are fully protected by an automatic sprinkler system.

In case of fire, water can be drawn at a rate of about five thousand gallons per minute for ten minutes, and two thousand gallons per minute indefinitely, the pressure being maintained constantly at one hundred and twenty-five pounds per square inch, automatically.

POWER-PLANT

The power-house, Building "E," Figs. VI and VIII, is a concrete brick and steel structure, seventy-eight feet in length by eighty-five feet in width, the boiler- and engine-rooms being separated by a brick fire-wall. The boiler-room is seventy-eight feet in length by forty feet in depth, the height to bottom chords of roof-trusses being thirty-five feet. The steam-plant consists of four water-tube boilers of two hundred horsepower each, in double settings, and at the rear of the boilers is a brick smoke-duct leading directly to the economizer, thence to the steel stack, which is of earthquake-proof design and construction, being one hundred and fifty feet in height and having a six-foot flue.

The main steam-pipes from each boiler are fitted with automatic "non-return" stop-valves and lead to the steel steam-header which is fourteen inches in diameter and is supported on brackets fixed to the fire-wall. At one end the diameter of the header is reduced to six inches, at which point a tee-connection furnishes steam for the power-house auxiliaries, and beyond this is a reducing-valve by means of which the pressure is reduced to about seventy-five pounds per square inch for the general factory supply, the boiler-pressure being one hundred and twenty-five pounds, with superheat as desired. At the north end of the boiler-room are the feed-pumps, one of which is kept in reserve.

A spur of the railway, to be described later, runs the full length of the room in front of the boilers and



FIG. V—OFFICE, LABORATORY AND SHOPS



FIG. VI—NITRIC ACID PLANT AND POWER HOUSE



FIG. VII—STOREHOUSES AND REFECTORY

is used for the removal of ashes; between the rails is an iron-covered duct in which the blow-off and other pipes are laid. The coal-bunkers are built outside the boiler-room wall at the west end of the building, and are so constructed that the coal is delivered on the boiler-room floor by gravity. They are supplied by means of an elevated railway.

The power-generating plant consists of three units of one hundred and twenty-five k. w. each, the engines being tandem compound condensing and directly connected to the generators, the current being 220 volt, direct. These units and the switchboard, consisting of three main and six distributing panels, are contained in a room seventy-eight feet in length by forty-five feet in width and thirty feet in height to bottom chords of roof-trusses. A 15-ton crane, having a span and travel equal to the width and length of the room, is also provided, and in one corner of this room is a hatchway 12 feet \times 12 feet, with steel cover, through which any of the auxiliaries may be lifted from the basement. In an opposite corner of the room is a rectangular opening through which the hydraulic accumulators project.

In the basement are located three jet condensers, a compound fire-service pump having a capacity of sixteen hundred gallons per minute at a pressure of one hundred and twenty-five pounds per square inch; two motor-driven hydraulic pumps and three air-compressors, also motor-driven.

STEAM AND POWER TRANSMISSION

The steam transmission structure consists of steel poles embedded in concrete, supported on piles, the poles being connected at the tops by inverted steel trusses and the pipe carried by yokes or cradles attached to the trusses and the tops of the poles. The pipe is insulated with asbestos-magnesia mixture, wrapped bandage-wise with hemp fabric payed with asbestos paint and is protected from rain by galvanized iron covers of semi-circular section coated with coal-tar. The average span between poles is about twenty-five feet and the height about sixteen feet. Condensation is removed at suitable points by means of automatic traps. The pipe varies in size from 5 inches in the mains to 2 inches in some of the laterals, the total length of the outside transmission-lines being about twelve hundred feet. Expansion-joints are inserted in the pipe-lines at proper intervals, and there are also suitable cut-off valves at each building and at various points in the main lines.

The steel poles which carry the steam transmission lines also serve for supporting the electric transmission wires. Brackets made from steel angles are clamped to the poles and the insulators are bolted to these brackets. The main switchboards, through which current enters each building, are located in asbestos-lined boxes attached to the outside walls and all circuits in each building are controlled from these switchboards. All motors are of the full-inclosed type and practically all wiring, especially in buildings where there might be any danger of fire from short circuits or sparking, is lead-inclosed, the lead casing being properly grounded.

Japan has no board of fire underwriters, but the government regulations in regard to electric wiring are, if anything, more severe than those of our board of fire underwriters, being in some respects irrational, and are as unalterable as the laws of the Medes and Persians, no matter what the conditions or circumstances may be.

HYDRAULIC SYSTEM

In the manufacture of celluloid the question of hydraulic pressure is very important, because this power is used in many of the operations connected therewith. In this plant a double system was adopted; namely, a low-pressure system working at five hundred pounds per square inch, which is used for filling and closing the presses, and a high-pressure system working at thirty-five hundred pounds per square inch, by means of which the final working-pressure is applied. Pressure is supplied by two pumps located in the basement of the power-house, which have been mentioned above. These are horizontal, double-acting pumps, motor-driven, with one gear reduction, each pump having a high-pressure and low-pressure cylinder. They are driven at sixty-five revolutions per minute, at which speed the low-pressure cylinder supplies fourteen gallons per minute, at 500 pounds per square inch, and the high-pressure cylinder four and one-half gallons per minute at 3,500 pounds per square inch. The pressure is maintained by means of two accumulators, the ram of the low-pressure accumulator being fourteen inches in diameter and having an effective stroke of twelve feet, while the ram of the high-pressure accumulator is five and one-half inches in diameter and has the same stroke. The stroke of the accumulators is controlled by means of automatic pilot-valves which cause the pumps to by-pass when the stroke desired is obtained; and there are also automatic switches by means of which the motors are stopped should the pilot-valves fail to work. In case both these devices should fail, the rams of the accumulators contain passages through which the water can escape should they exceed a safe working-stroke. The main hydraulic pipe-lines are fitted with shock-valves. All stop- and check-valves are of bronze, and all fittings such as elbows, tees, unions, etc., are of steel. Under ordinary conditions, one of these hydraulic pumps has sufficient capacity for the requirements of the factory, but at certain times both pumps are kept running in order to insure a constant supply in case of accident to either.

NITRIC ACID PLANT

In Japan, concentrated nitric acid is not an article of commerce; hence, in order to insure a supply, it was necessary to install a plant for its manufacture. A double Guttman battery, with some modifications by the writer, was installed in Building F (see Figs. I and VI). This plant has a capacity of about five thousand pounds of acid containing from 90 to 95 per cent. HNO_3 , per day of twenty-four hours. The building also contains tanks and apparatus for the storage of sulfuric acid and for making mixed acid. The smoke- and fume-ducts are lined with acid-proof

tile and lead to a brick stack of circular section, which is seventy feet in height and lined with heavy acid-proof pipe of 24-inch internal diameter. The mixed acid produced is blown by air-pressure through an iron pipe-line to Building No. 1 (the nitrating building), a distance of three hundred feet.

NITRATING BUILDING

Building No. 1 (see Figs. I and IV) is devoted to the nitrating of tissue-paper and to the washing and pulping of the resultant cellulose nitrate. This building consists of two parts, main building and lean-to. The main building has two floors, while the lean-to has first floor and basement. On the ground floor

The present capacity of the plant is two hundred and seventy pounds of cellulose nitrate per hour, and the entire nitrating apparatus is contained in a room measuring only 18 feet \times 20 feet. The nitrating-room is so constructed that a pressure slightly below the atmospheric is maintained therein, and all fumes are immediately removed through proper ducts by means of the two exhaust-fans located on the floor below and passed through two stoneware absorbing-towers outside the building. The cellulose nitrate is separated from the spent acid by means of the centrifugal machine, is then submerged in a large quantity of water and passes with the overflow water



FIG. VIII.—WEST END OF POWER HOUSE, SHOWING FUEL SIDING

of the main building, the room to the north is fitted for the storage and mixing of acids, while the room to the south contains the pressure-filters, by means of which the water used for washing the cellulose nitrate is purified; two 80-inch aluminium exhaust-fans; a pump and tank for supplying hot water for tempering the nitrating acids; auxiliary acid tanks and a centrifugal machine for separating the spent acids from the nitrate. On the upper floor of this building, one room is devoted to the storage and preparation of the tissue-paper to be nitrated; another room is used for weighing acids for mixing, while the rear room contains the nitrating apparatus which is so designed that all operations are performed mechanically, there being no handling of either acid or paper.

to the lead-lined tanks situated on the first floor of the lean-to of this building. Each of these tanks has a capacity of about two hundred pounds of cellulose nitrate, and when one has been filled the stoneware spout leading from the drowning-tank on the floor above is shifted, so that it discharges into the other of these tanks. The nitrate contained in the full tank is then roughly washed, the water drawn off and the product removed to other washing-tanks, where it is further washed and treated to perfect neutrality. These washing-tanks are fifteen feet in length and five feet in width, containing water to a depth of three feet, when filled. They are provided with mechanical agitators and resemble, in appearance, the beating-engines used in paper-mills. The first floor of the lean-to contains three of these washing-

tanks, in addition to the two lead-lined tanks used for the primary washing, and in the basement are located five more.

In the room on the first floor at the north end of the lean-to is located the pulping-machine, by means of which the nitrate is ground to a coarse pulp. It is then dumped into a hopper in front of the pulping-machine, this hopper being provided with screens by means of which the excess of water is drawn from the pulp, the mouth of the hopper being located in the basement. In this basement three pulp-centrifugals are installed, the baskets of which are lifted and run by means of a trolley to the mouth of the hopper, where they are filled with pulp, properly packed, trimmed, run back to the spindles and the water separated. The pulp is then transferred from the baskets to large zinc-lined boxes which, when filled, are carried by means of a truck to a hydraulic lift, raised to the first floor and transferred to Building No. 2.

The spent acid resulting from the nitration, after separation by the acid centrifugal, is returned to the tanks where it is built up or strengthened and used again immediately, no waste acid whatever being produced.

MIXING, CAKING AND DRYING

Building No. 2, in which these operations are performed, is thirty feet in width by eighty feet in length inside and has ground floor and basement, each of which is divided into three rooms by means of transverse fire-walls. On the ground floor, in the room at the south end, are located two mixing-machines where the pulp, as received from Building No. 1, is mixed with camphor and other ingredients, as required. This mixture is then transferred to the middle room on this floor, where it is pressed into thin cakes by means of automatic caking-presses of original design, the cakes being about twenty inches square and three-eighths inch in thickness. These cakes are then placed in a telescopic bronze frame, absorbing-pads and Tobin bronze plates being inserted between the cakes until the frame is filled, the pile of cakes thus formed measuring about four feet in height. The frame thus filled is then locked, inserted in a large hydraulic press, also of original design, capable of exerting a total pressure of about 1,500 tons, pressure is gradually applied and the excess of water contained in the mixture is expressed. The frame is then removed from the press and the cakes are next placed in hydraulic presses in the third or north room of this floor, absorbent paper being inserted between the cakes, pressure is applied and the cakes of material are allowed to remain in these presses for twenty-four hours, with several changes of absorbent paper. The absorbent paper used for this purpose is dried by passing through an automatic drying machine situated in the basement of this building, where it is perfectly and rapidly dried and returned to the floor above. In this building all material is handled by means of overhead trolleys traveling on I-beam tracks, the hoists having a load capacity of two tons. The only power required in this building is that which is employed for driving the mixing-machines and the

fan connected with the paper-dryers. These motors are of the full-enclosed type and are situated in the basement, motion to the mixing-machines being transmitted to the upper floor by means of vertical shafts.

GRANULATING

After the mixture above described is sufficiently dried, the cakes are removed to Building No. 7. This building measures 15 feet \times 20 feet in plan and contains first floor and basement. The first, or ground floor, is divided into two rooms 10 feet \times 15 feet in size, in which are situated two machines for reducing the cakes of material to a granular condition. This operation is somewhat hazardous under ordinary conditions, but in the present instance practically all danger of fire or explosion has been eliminated by the use of machines and auxiliaries of original design. The motors which drive these machines are situated in the basement, but are controlled from the floor upon which the machines are situated.

DIGESTING AND CONVERTING

Up to this point the product in its physical appearance somewhat resembles cakes of wood-pulp and consists of an intimate mixture of cellulose nitrate, camphor and such other substances as may have been added to produce the kind or quality of material desired, and it is now ready for conversion into celluloid. For this purpose it is transferred to Building No. 4 (Figs. I and III). This building consists of first floor and basement, is 30 feet \times 80 feet in plan and each floor is divided into four rooms by means of transverse fire-walls. On the first floor, the room to the north contains two mixing-machines driven by motors situated in the basement. The granulated mixture is placed in these machines, the proper weight of alcohol added and the mixture agitated until the alcohol is perfectly blended, after which the mixture is transferred to air-tight containers in which digestion is allowed to proceed for about twenty-four hours, at the end of which time the mass is subjected to mastication in rolling and other machines of special design. These machines are contained in three fire-proof rooms in this building and are driven by vertical motors which are situated in the basement and controlled by the operators at the machines. The final result of this operation is crude celluloid in thick sheets, in which condition it is transferred to Building No. 3.

WELDING AND SHEETING

In this building (No. 3) the sheets of raw material, as received from Building No. 4, are placed in sectional steel moulds, as many sheets as are necessary for forming a cake of the required weight being employed. After being closed, three of these moulds are inserted in each of the two welding-presses by means of electric cranes, each of these presses being capable of exerting a pressure of three hundred tons. The material is kept under pressure in these moulds for about four hours, being first heated by means of hot water circulating through the moulds and then cooled. The moulds are then removed from the presses and, when opened, the material is found in the form of a cake

weighing from one hundred and fifty to two hundred pounds. This cake is then transferred to the middle room of the building, where it is cut into sheets of any desired thickness by means of two automatic sheeting-machines, after which it is placed in the drying or seasoning compartments in Buildings Nos. 9 and 10. The room at the south end of the building is devoted to the manufacture of tubes and rods and contains three large extruding-presses of original design.

SEASONING

Buildings Nos. 9 and 10 (Fig. IV), each of which is 30 feet \times 80 feet in plan, are of special design and construction. In the seasoning of celluloid it is necessary that great care should be exercised in order that the material may not be distorted and it is also necessary to guard against the danger of fire and to so protect the buildings, that in the event of a conflagration the rest of the plant may not be endangered. Also to so construct the buildings that the material may be seasoned in the shortest time consistent with quality and to avoid keeping an unnecessarily large stock on hand.

Each of these buildings is divided by means of transverse fire-walls into five rooms, the one at the south end of each being subdivided by a short longitudinal wall into two rooms, one of which contains an exhaust-fan and its necessary motor. Outside each building and extending the full length thereof at one side is a concrete duct measuring 4 feet \times 4 feet in cross-section, the top of this duct being level with the floors of the rooms. At the south ends of these ducts, laterals of full cross-sections extend into the fan-rooms, an opening thereto being cut through the floors, and the large double exhaust-fans are set directly over these openings which form the fan intakes. Smaller laterals extend from the ducts into each of the rooms in which the material is dried, and are furnished with proper gates by means of which the air-pressure in any one of the vacuum chambers in which the material is placed, may be controlled. The reduction of pressure usually employed is about 2 inches. The doors of these buildings (each room having four such) have no latches or springs but are held very tightly closed by the suction. Each room in this building is virtually a fire-proof vault, and if a fire was to occur in one of these rooms, there would be comparatively little danger of the ignition of the contents of the other rooms. Heat is supplied by overhead coils and fresh air is taken in from above, thus reversing the usual conditions obtaining in the drying of such materials. Each room has a liberal supply of automatic sprinkling-heads.

The dried sheets of material produced are absolutely flat and the system has proved to be very satisfactory in operation. Each building has a capacity of about one hundred thousand pounds of material, the comparatively large capacity being due to the fact that fully 90 per cent. of the celluloid used in Japan is about $\frac{1}{8}$ inch or more in thickness.

FINISHING

After the sheets of material are dried or seasoned,

they are removed to Building No. 5 (see Figs. I and III), where they are finished or polished. This building is also 30 feet \times 80 feet in plan and has ground floor and basement. On the ground floor is situated the large 1,200-ton finishing press, capable of finishing twenty sheets of material at one operation. The basement contains buffing and nickel-plating apparatus, by means of which the plates used in this operation are finished; and there is also a heavy rolling-mill for the same purpose.

STOCK ROOM

After polishing, the material is removed to the stock-room, Building No. 6 (Figs. I and V), also 30 feet \times 80 feet in plan, which has ground floor and basement and is furnished with the necessary racks, shelving, etc., for the storage of the finished stock. In this building the material is packed for shipment, the cases removed to a branch of the small railway near at hand and thus taken from the plant for shipment.

OTHER BUILDINGS

The foregoing description includes all buildings devoted solely to the manufacture of celluloid. The laboratory; designing and color building; machine, carpenter and pipe-shops; and the office are shown (from left to right) in Figs. II and V. These buildings, with the exception of the designing and color building, have two floors and basements. In the laboratory, Building "D," the ground floor is divided into three rooms, one of which is an office, another a stock-room for chemicals and the third is devoted to operations requiring the use of furnaces, etc. On the second floor, the front room is used for general experimental work, the middle room for the storage of apparatus, while the two rear rooms are used for analytical work. The basement contains water-still, furnaces, etc., and is also used for storage.

The designing and color building, "C," consisting of first and second floors, is really a celluloid plant in miniature, and all operations performed in the main plant can be reproduced here on a small scale. This is of inestimable value in an industry of this character, in which new materials and new effects are constantly required; with the facilities afforded by this miniature plant, results are obtained very quickly and at a minimum cost. This building also contains the machinery necessary for grinding the pigments used in the manufacture of the material in the main buildings and, on the second floor, all dyes required are also prepared.

Building "B," the machine-shop, consists of two floors and basement, the latter being the pipe shop and containing the necessary tools, such as pipe-cutting and threading machines, a power hack-saw, full outfit of taps and dies of all sizes, etc. As the total length of pipe of all sizes used in the plant amounts to something over ten miles, there is, of course, constant need for repair.

The second floor contains the machine repair shop and has a full outfit of modern, motor-driven machine tools, including lathes, a 30 inch \times 30 inch \times 10 foot planer, a milling-machine, radial and speed drills,

grinders, shaper, etc., and has two overhead traveling cranes running the full length of the building.

On the upper floor is situated the carpenter-shop with a few necessary wood-working machines, such as surfacing planer, hand planer, circular saws, lathe, boring machines, band-saw, etc., all machines being motor-driven. The facilities for repairs afforded by this building have resulted in great saving, both in material and time; because in Japan it is impossible to have a repair job done quickly and when it is finished the chances are that it is not properly executed.

The office, Building "A," has two floors and basement, the interior being of conventional design.

The ice-making plant, Building "G" (including storage room), is 20 feet X 40 feet in area and has a capacity of one ton per day.

A blacksmith's shop, Building "V," is also provided

All buildings thus far described are situated on the raised or filled portion of the land, the elevation being 12 feet above the general level of the ground. The lower level, upon which are situated storehouses, etc., is reached from the elevated portion by means of a granite stairway situated in front of Building "A," and also by means of an inclined plane 12 feet in width and 70 feet in length, the lower end of which may be seen in Figs. II and V. This inclined plane has granite retaining-walls and is paved with granite flags laid in concrete.

Upon the lower level are situated Buildings "I," "J," "M," "N," "O," "P," "Q," and "R" (see Figs. II and VII). Of these, Building "Q" is the gatekeeper's lodge; "R" is the wardrobe in which the workmen change their clothing, as is customary in Japan; "I" and "J" are brick storehouses in which alcohol, tissue-paper and camphor are stored; "M" is the workmen's refectory (also a peculiarly Japanese institution); and "N," "O" and "P" are storehouses of corrugated iron with concrete foundations and cement floors. Of these buildings, "N" contains the stock of sodium nitrate; "O" is a storehouse for spare parts, pipe-fittings, etc.; and "P" is the pattern storehouse. All these storehouses are reached by a loop of the railway, as shown in Fig. I.

There is, of course, a very perfect electric lighting system including twenty arc lights, at various points, for outside illumination.

The total cost of the plant was about one million dollars. This plant has been in operation for about a year and up to the present time the results, all things considered, have been satisfactory, notwithstanding the troubles which are inseparable from a lack of skilled labor. Within about nine months after the inception of operation, the plant was producing material to the extent of about eighty to eighty-five per cent. of its capacity, and it is very gratifying to state that not a pound of unmarketable material has been produced. When we consider that the majority of the operatives (many of whom had never even seen celluloid) were recruited from the lower classes (wages averaging about forty cents per day) and that they were totally unfamiliar with the operation of machinery

the showing which they have made has been very satisfactory.

SAKAI, JAPAN

RECENT DEVELOPMENTS IN THE ELECTRIC STEEL FURNACE¹

By P. L. V. HÉROULT

The progress of the electric furnace for refining steel during the last year has been characterized by a steady improvement in established methods and a reduction in costs rather than by the introduction of any new processes or radical alterations in furnace construction.

The electric steel furnace has now reached a point where the reduction of costs depends entirely on improvements in detail both in furnace construction and manipulation. It may now be said that "the general principles of electric refining have been so clearly established that it is now possible to determine those furnaces which are destined to play an important part in the metallurgy of iron and steel."

The growth of the electric process is shown by the following statistics of the output of electric steel in three countries:

	1909	1910
Germany.....	17,773	36,188
Austria-Hungary.....	9,048	20,028
United States.....	22,997	55,335

In Europe the process was developed further for high-priced steels but in the United States the principal problem has been that of making rails. The present position has been admirably summed up by Mr. W. R. Walker. He stated recently in New York that "his investigations lead him to believe that the so-called heavy products could be made in the electric furnace, in conjunction with the acid or basic Bessemer at a cost that would not be prohibitive and that the steel so produced would be exceedingly low in oxygen and other impurities."

He further pointed out that "his investigations are based on the operation of two fifteen-ton furnaces for a period of three years, and on 5600 tons of rails which have been in the track for more than two years under hard conditions of service." He stated, "that although exposed to extreme cold as low as 52° below zero, no breakages have been recorded and that electric steel is denser than basic and open-hearth and Bessemer steel and that no oxides or slag enclosures can be detected at a magnification of 1000 diameters." He further pointed out that "electric steel can be made with smaller additions of manganese and equal wearing properties can be obtained from an electric steel containing about 0.08 per cent. less carbon than a similar open-hearth steel, thus reducing the risk of breakage, without sacrificing wearing qualities."

At the present time the application of the electric furnace for the manufacture of intermediate steel, and all qualities of alloy and special steels is established; and the application of the electric furnace for these purposes has been so clearly proved successful

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

that it is only a question of time before the general application of the process will become not only advantageous but absolutely necessary to compete in this class of trade.

The quality of castings made in the electric furnace, especially for automobiles and for all kinds of machine parts, is superior to that made by any other process, while the cost of steel refined by electricity as compared with that made by the crucible process is so much lower that it enables castings of crucible steel quality to be made at a price about the same as those made from the highest quality acid open-hearth steel. The importance of this cannot be overestimated in the machine shop, for it often happens that several hundred dollars worth of machine work will be put into a casting before the blow-holes and other defects can be detected. By the use of the electric furnace the quantity of blow-holes and waste can be reduced to a minimum, and saving in the cost of machine work alone would justify paying a very much higher price for electric steel castings, if this were necessary.

In the case of many low-carbon high-quality castings made in the electric furnace, it is unnecessary to anneal them, and this makes an additional saving in the cost of manufacture.

The following tests were given by ordinary mild steel castings from an electric furnace:

ELECTRIC STEEL CASTINGS

Analysis: carbon, 0.12 per cent; manganese, 0.4 per cent.; silicon, 0.2 per cent.; sulphur and phosphorus, below 0.02 per cent.

Test No.	Area sq. in.	Reduction area Per cent.	Elastic limit per sq. in.	Ultimate strength per sq. in.	Elongation diam. $\frac{1}{8}$ " Per cent.
			Lbs.	Lbs.	
36138	0.2454	39.5	45,696	71,456	3"—28.75
36139	0.2359	53.2	33,376	63,616	3"—35.00 12"—34.00

From these figures it will be seen that it is possible to make a mild steel casting comparing favorably with plate steel, and the question arises whether the working of steel under the hammer or rolling mill can improve its quality in any way whatever if the steel be free from faults and cavities.

Another application of the electric furnace which is of great importance to manufacturers of alloy steel depends upon the fact that any quality of scrap can be worked up and the valuable metals retained. Thus, for example: It is not uncommon practice to melt up charges of miscellaneous tungsten steel including various tools, turnings, hammer scale and "spillings" from crucibles, all of which contain a certain quality of tungsten. Such a charge can be melted up, and the necessary additions made to bring the composition up to the required specification.

Another case of this kind is the manufacture of chrome nickel and vanadium steels for automobile work, etc., from miscellaneous scrap containing unknown quantities of nickel and chrome and vanadium. Such scrap is often sold at a low price, owing to the loss in remelting by ordinary methods and on account of the very large percentage of scrap in ornament and other works, where government specifications and other reasons cause excessive scrap production. It is not

uncommon to melt up such a miscellaneous charge and take bath samples, make the necessary analysis in forty minutes, and add the necessary alloys for the steel required.

With regard to the reduction in cost, which has been effected during the last few years, it may be said that this is almost entirely due to slight improvements in practice and design which are the results of continuous experience. Two years ago it was considered good practice to melt and refine steel scrap in six hours at a power consumption of 750 kw. hrs. per ton, whereas, at present, furnaces are working steadily carrying out the same operation in four hours at a power consumption of under 600 kw. hrs. over periods of six months. Similar reductions in operating expenses have been made in all other details, such as labor charges, refractories, etc.

With reference to the question of refining large ton-nages of steel, a great deal of work has been done during the last two years, but the conditions are more complicated and the economical questions have to be considered with great care in each special case. Thus, for instance, in Germany, where 95 per cent. of the output of steel is made by some basic process and the ores are such that they are entirely dependent upon the basic bessemer process for the cheap production of steel, the application of the electric furnace will be found in the refining of steel which has previously been treated by the basic bessemer process. Steel made by this process is not sufficiently uniformly reliable to meet the requirements of modern engineering, and the German steel makers find themselves faced with the necessity of abandoning the basic bessemer process on which they are dependent for cheap steel or for adding electric refining to their present process. Several furnaces have been operated in this way for the last twelve months and the results are so satisfactory that furnaces of 25 tons capacity have just been put into operation to work in conjunction with basic converters of the same capacity. In this way a steel superior to the basic open-hearth product will be made at a cost which will probably be not much greater after the furnace has been running for twelve months and the plant is brought up to full capacity.

The progress of electric steel refining has been retarded considerably by the large number of unsuccessful furnaces that have been erected by men who possess no special knowledge of electric furnace work or the steel trade, and considerable quantities of inferior steel have been turned out in the past as a result of this. To erect and operate an electric furnace successfully it is essential to have had considerable experience, both in the steel trade in general and in electric furnace work in particular, as the old established principles of steel-making cannot always be followed. As progress continues and operating expenses are reduced, a continually widening field for the process and a cheapening of the best qualities of steel will result together with an improvement of the quality of castings and other materials which can be manufactured at a low price.

Time has also eliminated many difficulties and fallacies relating to electric furnace work, so that it is now easier for the steel maker to decide the type of furnace he should adopt and to undertake the manufacture of electric steel with complete confidence.

NEW YORK CITY

AN ELECTRIC HEATER FOR LABORATORY DISTILLATIONS

By L. T. BRYSON

Received September 11, 1912

While the heater described below was designed only for naphtha and turpentine distillations, it has been found so useful for miscellaneous extraction work, moisture determinations, etc., that details of its construction may be of interest. It may be set up in almost any laboratory with very little expense.

A steel can $4\frac{1}{2}$ inches in diameter and 9 inches high, with a $\frac{3}{8}$ inch vertical slot cut half-way down the side, is lined with a double thickness of $\frac{1}{16}$ inch asbestos paper. About $\frac{3}{8}$ inch of loose magnesia is placed in the bottom and covered with a circular piece of heavy asbestos board or transite. The can is supported on a ringstand in the usual way.

The heating element is composed of 9 feet of No. 33 nichrome wire—for 220 volts—which is wound on a block of transite $\frac{1}{2}$ inch thick, 2 inches wide and 3 inches long, having holes drilled for a bolt at each end and shallow notches cut along each of the long edges, about $\frac{1}{8}$ inch apart, to receive the wire. To give greater effective radiation the center of the block is cut out as shown by dotted lines (Fig. 1).

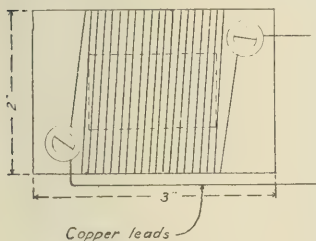


FIG. 1—DETAIL OF ELEMENT

Each end of the resistance wire is fastened, together with the end of a piece of No. 16 copper wire, under a No.

6-32 bolt passing through the corresponding end of the block. The complete element is placed in the

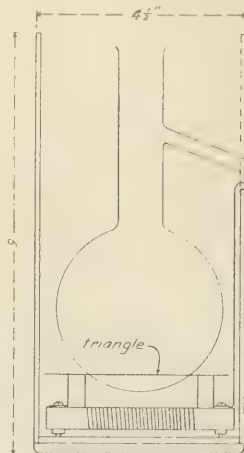


FIG. 2—SECTION OF HEATER

asbestos.

With the dimensions given above, the heater will accommodate a 250 cc. flask, and gives distilling vapor temperatures up to 300° C. when the flask is supported about $\frac{1}{2}$ inch above the element by means of a triangle. With the flask in place the can should be fitted with a cover perforated for the thermometer, thus enclosing the entire neck of the flask and part of the side-tube; the distillation characteristics are then very constant. With a rheostat having steps of equal resistance, as above, the temperature increment per step necessarily varies from a minimum value at the lower temperatures to the maximum value on the last points. A temperature increment which would be constant throughout the range was not considered desirable for this work.

NORTH WORKS
ILLINOIS STEEL CO.
CHICAGO

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The Fifth Annual Meeting of the American Institute of Chemical Engineers was held in Detroit, December 4th to 7th.

At the first business meeting the following officers were elected for the ensuing year:

President—Dr. T. B. Wagner, Corn Products Refining Company, New York.

First Vice-President—M. C. Whitaker, Professor of Chemical Engineering, Columbia University, New York.

Second Vice-President—Richard K. Meade, General Manager, Tidewater Portland Cement Company, Baltimore.

Third Vice-President—G. W. Thompson, Chief Chemist, National Lead Company, Brooklyn.

Secretary—J. C. Olsen, Polytechnic Institute, Brooklyn.

Treasurer—F. W. Frerichs, Manufacturing Chemist, St. Louis.

Auditor—Geo. D. Rosengarten, Vice-President, The Powers-Weightman-Rosengarten Company, Philadelphia.

Directors—Geo. D. Rosengarten; Jokichi Takamine, Consulting Chemist, Parke Davis & Company, Detroit; Jas. R. Withrow, Professor of Industrial Chemistry, Ohio State University, Columbus.

Dr. T. B. Wagner was elected President of the Institute to succeed Dr. L. H. Baekeland. Dr. Wagner was born in Chicago, in 1868. He was educated at the Universities of Freiburg, Würzburg and Basel, where he studied natural sciences and chemical technology, has had an interesting and successful career as a chemical engineer and has been prominently identified with the starch and sugar industries of the country for many years. He served two years as chemist and assistant superintendent of the National Linseed Oil Company, three years as a member of the firm of Wagner & Jussen, Chemists and Engineers, of Chicago; two years as manager for the Louisiana Sugar Industry; two years as Chemist for the Glucose Sugar Refining Company; one year as Assistant General Manager of the Glucose Sugar Refining Company; one year as General Superintendent of the Glucose Sugar Refining Company; one year as General Superintendent of the National Starch Company; four years as General Superintendent and Director of the Corn Products Refining Company; and for the past six years as Secretary of the Operating Committee of the Corn Products Refining Company. Dr. Wagner is at present one of the managers of the Corn Prod-

ucts Refining Company and is now stationed at the home office of the latter corporation at 17 Battery Place, New York. Dr. Wagner's most notable chemical engineering work was that in connection with the wonderful new plant of the Corn Products Refining Co. at Argo, Illinois.

The Institute visited many of the important industrial establishments in the neighborhood of Detroit under the general direction of a local committee composed of Mr. L. D. Vorce, General Superintendent of the Pennsylvania Salt Company, and Mr. R. A. Plumb, of the Trussed Concrete Steel Company. This local committee was assisted by the Society of Detroit Chemists.

The Institute was particularly fortunate in seeing some of the most highly developed industrial and engineering plants in the neighborhood of Detroit. They visited the laboratories and works of Parke, Davis & Company, Ford Motor Company, Acme White Lead & Color Company, Pennsylvania Salt Manufacturing Company, Berry Bros., Ltd., Detroit Sulphite Fibre Company, Detroit Copper and Brass Rolling Mills, Michigan Malleable Company.

The laboratories and buildings of The University of Michigan were inspected by the Institute under the guidance of Professors Campbell and White. The members were also entertained at luncheon by the University authorities where they were cordially welcomed by President Hutchins.

Many interesting and important papers were presented, the majority of which will be printed in full in subsequent issues of *THIS JOURNAL*. Brief abstracts of some of the papers follow:

Protection of Intellectual Property in Relation to Chemical Industry. Presidential Address. By L. H. BAEKELAND.—This address is printed in full on page 51 of *THIS JOURNAL*.

Changing the Rate of Setting of Portland Cement. By E. E. WARE.—A report on the commercial manipulation of 100,000 bbls. of quick-setting Portland cement clinker. This clinker was the product of a mill, operating on marl, and following the practice of storing large quantities of clinker, as well as ground cement, for use in supplying the early spring markets. Ordinary methods of retarding had no effect. Additions of plaster, calcium chloride, or slaked lime failed to change the rate of set. However, a small amount of hydration of the material, either in course of grinding or after grinding, was sufficient to enable the normal amount of plaster to perform its proper function of retardation. The actual method of manipulation was to heat the clinker to approximately 100° C., which temperature was high enough to drive off part of the water

from the added gypsum, which water proved sufficient for the purpose.

Industrial Efficiency in Chemical Manufacture. By WM. M. BOOTH.—This paper discusses the various phases of the problems arising in connection with the choice of site, erection and operation of manufacturing plants. The author submits classification as a basis for the analysis of such enterprises and proposes that this method of analysis be applied for the purpose of determining the value of a proposed business or the prospects of a going business. The fundamental idea behind the classification is a careful investigation of existing conditions, costs, etc., to serve as a starting point.

Technical Accounting and Chemical Control in Sugar Manufacture. By DAVID L. DAVOLL, JR.—A brief sketch of the process of manufacture of cane and beet-sugar; a glossary of terms most generally used in sugar houses in the United States and Cuba; collection and preparation of samples for analysis; the several analyses needed, reasons for making such analyses and methods of carrying out the same; preserving and compositing samples. The semi-monthly Chemical Statement. Some approved machines for preparing samples and apparatus for carrying out the control. General adoption of Technical Accounting and fully recognized necessity for efficient chemical control. Some problems requiring much further chemical investigation.

Availability of Blast Furnace Slag as a Material for Making Brick. By A. E. WHITE.—An extensive series of experiments shows that a very excellent grade of brick can be made from blast furnace slag in combination with lime and other materials commonly used in this process.

The Chemical Engineering Laboratories and Courses at Columbia University. By M. C. WHITAKER.—Outline of the recent adoption by the engineering faculty of Colum-

bia University of a new three-year post-graduate course in engineering; detailed description of the chemical engineering curriculum on the graduate basis; the essential features of the undergraduate course leading to post-graduate work in engineering; general description of the fundamental principles of the chemical engineering course at Columbia; description illustrated with lantern slides showing specific installations such as filter presses, precipitation tanks, centrifugals, multiple effect vacuum evaporators, vacuum chambers, column distillation and extraction, pulp digesters and paper beaters, electrochemical equipment, etc.

Tests on the Opacity and Hiding Power of Pigments. By G. W. THOMPSON.—This paper gives a description of an ap-



DR. T. B. WAGNER, PRESIDENT-ELECT AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

paratus used for testing the opacity and hiding power of pigments mixed with oil on standard formulae where the thickness of the liquid paint film is controlled and measured. Calculations are given, showing coefficients of opacity.

Solvents for Acetylene. By J. H. JAMES.—The first part of the paper details the laboratory apparatus and methods used in making the absorption tests. The results obtained with various solvents are tabulated and discussed at some length with reference to the possible connection between solvent power and chemical composition of solvent, the theory being advanced that all high absorption represents true chemical action between the solvent and the acetylene. Finally, the advantages of acetaldehyde as an acetylene solvent for industrial use are discussed, and curves and data giving the results of several industrial scale experiments with acetaldehyde and two other solvents are shown.

The Bituminous Rocks of the United States and their Use for Street Surfaces. By S. F. PECKHAM.—A description of the author's trip last summer, taking in Chicago, McAlester and Ardmore in Oklahoma, Ft. Worth, Los Angeles, Santa Barbara, San Francisco, Salt Lake City, Denver, Kansas City, Louisville and Washington, D. C. Careful observation of the asphalt streets in all these cities showed widely varying conditions. On the Pacific coast the pavements were maintained at great expense and in fine condition from residuum of the petroleum so abundant in that locality. In Ardmore, Ft. Worth and Kansas City, streets have been laid of the natural rock asphalt found in the neighborhood of Ardmore, Okla. A Fort Worth street, one mile long, that had been laid three years, was in perfect condition with not a contraction crack after the excessive cold of the previous winter. Ardmore streets, after six years, looked as if they had just been vacated by the workmen who laid them. Kansas City streets, after fifteen years' use, with no expense for repairs, were found in as good condition as most of the New York City streets laid not more than two years ago. There are some very pertinent remarks concerning the neglect of streets in the Eastern cities that might be laid from this material which is so abundant in Oklahoma that the supply has been described by the State Geologist as sufficient to pave all the cities of the United States. Very pointed questions are asked concerning the neglect by the authorities of our Eastern cities of these sources of a material which is among the best in the world for street paving.

Report of the Patent Committee. By DR. GROSVENOR, Chairman.—"The part which the American Institute of Chemical Engineers has so far taken in the agitation for better patent service has been so prominent and its effect in bringing the organization before men of importance throughout the country so considerable, that an earnest appeal is made for the continu-

ance of this work in a manner even more active and aggressive than has been possible in the past.

"Largely through the generosity of our President, the Institute has sent out some 9,000 pamphlets to Congressmen, Senators, public officials, members of the Patent Law Association, Inventors' Guild, members of the Chemists' Club and to prominent manufacturing organizations. The number of readers that can be reached in this way, however, is extremely limited and the results obtained are somewhat temporary in character. We may interest a few influential men to urge their Congressmen to kill a particular bill or support the establishment of a particular court for patent litigation, but the next Congress or even the next Session is likely to make it necessary to do all our work over again, and repeated appeals of this kind become monotonous and ineffective. What is required is general public education, and this can be secured only through the public press rather than by writing papers for scientific journals or any such limited distribution as this organization can afford.

Such a campaign would cost approximately \$8,000 or \$10,000 for the first year, and there should be no difficulty in securing the financial support of the many corporations doing business in patented articles when such a campaign was once undertaken. Many of our members are vitally interested in patented goods and have sufficient influence with their companies to insure liberal subscription if the Institute were to undertake such a campaign. Our association hitherto with the patent agitation makes it extremely fitting that the Institute should do this if the members approve. Our retiring President has done most valuable work in this direction and, if he can give the time, would make a most fitting chairman of the Patent Committee.

"Your Committee, therefore, submits for your consideration the following resolution and retires with the earnest hope that the small foundation it has laid may be broadened and built upon to the permanent credit of the Institute:

"*Resolved*, That it is the desire of the members of the American Institute of Chemical Engineers in regular meeting assembled to organize on a large scale a campaign of public education with regard to the U. S. Patent System, its industrial value to the country, its preservation and perfection.

"That to this end, Dr. L. H. Baekeland is recommended to the President-elect for appointment as Chairman of the Patent Committee for the ensuing year.

"That the Patent Committee be authorized to receive subscriptions and be instructed to use its best ability and the means thus afforded, to institute an active campaign of public education throughout the country.

"That each member of the Institute be requested to present the financial needs of this Committee to the corporation or corporations with which he may be identified and to request the support of this work by these corporations."

ADDRESSES

PROTECTION OF INTELLECTUAL PROPERTY IN RELATION TO CHEMICAL INDUSTRY¹

By L. H. BAEKELAND

The mass of unthinking people, as well as those whose views are predominantly guided by precedent, have little or no conception of the natural rights of intellectual property. It is difficult to teach such people that adequate protection of intellectual property is abundantly more beneficial to the community at large than to the temporary individual possessors of these rights.

Yet these same people consider as sacred and inviolable any

other property rights as soon as the latter relate to chattels or real estate, whether such rights were obtained by purchase, by inheritance, by gift, by privilege, by labor, or in any other way.

Furthermore, the laws of all nations are very strict in protecting such property rights, but do not concern themselves, beyond certain limits, whether the possessor of the property is morally entitled to it or not. Neither do our laws concern themselves whether the owner uses his property for good or for wrong, for the benefit of the community at large, or for the gratification of his own selfish purposes. From the standpoint of the law (with very few exceptions, such as, for instance, Board of Health or police-ordinances, or cases of so-called

¹ President's address before the American Institute of Chemical Engineers, at the Detroit meeting, December, 1912.

eminent domain), it matters little whether the private ownership of some property is a burden to the community or whether it is an impediment to the happiness or the free development of its citizens.

Neither is there any dispute as to the time the ownership of such property should last. Except for restrictions put on ownership by taxes, property rights are practically perpetual, and can be transferred only by accepted methods as, for instance, sale, barter, inheritance, or donation.

In some rare instances, there may be expropriation for public purposes (or eminent domain), but even then, some suitable compensation is usually made.

All this is readily accepted as an axiom, as an underlying article of faith by all laws relating to property. Only the socialist dares dispute these rights, while even the single taxer admits them to such a decided extent that he desires to abolish taxes on all property created by labor or enterprise, so as to shift the burden of all taxation on unearned land values.

When, however, it comes to recognizing the claims of ownership to intellectual property, the result of the truly creative effort of the citizen, right away we butt against some stubborn conceptions, which have petrified into the code of our long established laws.

If Tom steals Dick's two dollar scarf pin, Dick will have little trouble in putting Tom in jail, even if Dick himself has obtained his pin by questionable methods. But when it comes to protecting, even for the short period of seventeen years, the most logical, the most legitimate personal property, intellectual property as embodied in patent rights, with all that it involves, with enterprises depending thereon, based often on the work of a lifetime, then our law courts are woefully deficient, on account of the uncertainties, delays and enormous expenses connected with the adjudication of patent rights. All this works overwhelmingly in favor of the litigant with the well filled purse, the large corporation.

Yet, no country in the world has expressed in a fairer and broader spirit the rights of intellectual property, than the United States, in Article I, Section 8, of the Constitution: "Congress shall have power to promote the progress of science and the useful arts by securing for limited times to authors and inventors, the *exclusive* right to their respective writings and discoveries."

This proclamation lifted the right of a patentee at once far beyond the mere privilege conferred by most other countries, which grant patents not only to the real inventors or originators, but also to those who are first to introduce unpublished inventions into their respective countries. With some legitimate pride, we can say that in this respect at least, American patent law stands head and shoulders above the laws of Germany, France and England.

The principles of the right of intellectual property so clearly defined in our Constitution were repeated in the preamble of the French Law of Jan. 8, 1791, which declares:

"The National Assembly, considering that every new idea whose manifestation or development may become useful to society belongs to him who conceived it, and that not to regard an industrial invention as the property of its author would be to attack the essential rights of man; considering at the same time how much the lack of a positive and authentic declaration of this truth may have contributed till now to discourage French industry by occasioning the emigration of numerous distinguished artists and by causing to pass out of the country a great number of new inventions from which the Empire ought to have drawn the first advantages; considering finally that all the principles of justice, of public order, and of national interest imperatively command that it determine for the future the opinion of French citizens with regard to this class of property by a law which consecrates and protects it. . . .etc."

The wisdom of these provisions has been abundantly proved by subsequent events. Only a man stubbornly blind to evident facts will deny that just those countries which have the most liberal laws for patent protection are also those which have taken the lead in the industrial and scientific development of the world. No man was more imbued of the benefits of the patent system than Abraham Lincoln, when in 1860, in his speech at Springfield, Illinois, he said:

"In the world's history, certain inventions and discoveries occurred of peculiar value, on account of their great efficiency in facilitating all other inventions and discoveries. Of these were the art of writing and of printing, the discovery of America, and the introduction of patent laws. . . . The patent system . . . added the fuel of interest to the fire of genius, in the discovery and production of new and useful things."

Up to about thirty years ago, our patent system covered tolerably well the purpose for which it was intended. It stimulated individual inventions and promoted numerous private enterprises. Since then, with the extraordinary growth of our nation, with the tremendous increase of agglomerations of capital for industrial enterprises, and more specially with the astonishing increase in the ramifications of applied science, our patent system has become totally inadequate to the needs of the country; it suits our new conditions in about the same way as baby clothes fit an overgrown boy.

Our patent system, although based on an excellent fundamental law, has now degenerated into a set of exceedingly complicated technicalities of law practice, a system of legal acrobatics, whereby any contestation before the courts can be turned into "perpetual motion" to the advantage of wealthy litigants, and whereby the individual patentees of slender means and the small industrial concerns find themselves under smothering disadvantages when opposing rich antagonists. In this way, our patent system, instead of accomplishing its intended purposes of stimulating individuality, simply reinforces the rich and big industrial enterprises, and discourages the individual inventor unprovided with a liberal bank account.

I shall not take up your time by repeating all that has been published lately on the subject, but refer you to the available printed publications: ["Abuses of our Patent System," L. H. Baekeland, *THIS JOURNAL*, 4, 333; "The Incongruities of Patent Litigation, Ditto, 4, 785. "The United States Patent System," Robert N. Kenyon, *Transactions of the American Institute of Chemical Engineers*, Vol. IV, 1911. "The Gist of the Supreme Court Decision in the Dick Patent Case, and of the Proposed Patent Law Amendments," Gilbert H. Montague, *The Engineering Magazine*, May-June, 1912. "The Sherman Anti-Trust Act and the Patent Law. The Supreme Court on Patents (The Dick Patent Case)," Gilbert H. Montague, *Yale Law Journal*, April-May, 1912. Report No. 1161, to accompany H. R. 23,417, August 8, 1912, Hon. W. A. Oldfield, Chairman of the Committee on Patents, Washington, D. C.]

It is true that on November 4, 1912, the Supreme Court of the United States has promulgated revised Rules of Practice for the Courts of Equity, which intend to simplify our methods of litigation. Unfortunately this is only a half-way measure, leaving still abundant opportunity for the tactics of delay, chicane, and expense which have too much disgraced American patent litigation.

These new rules might gain in efficiency, if they were supplemented by the creation of a final court of patent appeals. They might be made incomparably more efficient if they could be strengthened by a system whereby the adjudication of the validity of patents does no longer devolve upon judges who do not possess the technical or scientific preparation required nowadays for discerning the merits of complicated patent questions. Some of the far-reaching details of scientific technology absolutely

baffle the comprehension of those who have no preliminary technical or scientific training. Certain problems of chemistry and physics involved in many patent suits can no longer be understood by an intelligent judge, if he has not had long and systematic preliminary training in that branch of knowledge. I do not deny that an intelligent judge can be coached and instructed by long, tedious, time-robbing methods, even in intricate scientific problems; but his education has to be made over again for each special case. After you have made a chemist of him for one case, the next adjudication will require the knowledge of a physicist, an electrician, an engineer, and so forth.

What would any judge say of a chemist or a mathematician, or an engineer, totally ignorant of the practice of law, who tried to conduct a law case in court? Such an amateur lawyer might succeed in doing so, but to what hopeless loss of time, misunderstandings, and confusion would this lead before the subject had been mastered to some extent. Yet this is exactly what happens with a judge whom we entrust to decide on the validity of a patent involving highly intricate scientific or technical subjects.

Judge Hand expressed himself very eloquently on this subject: "I cannot stop without calling attention to the extraordinary condition of the law which makes it possible for a man without any knowledge of even the rudiments of chemistry to pass upon such questions as these. The inordinate expense of time is the least of the resulting evils, for only a trained chemist is really capable of passing upon such facts, *e. g.*, in this case, the chemical character of Von Furth's so-called 'zinc compound,' or the presence of inactive organic substances. In Germany, where the national spirit eagerly seeks for all the assistance it can get from the whole range of human knowledge, they do quite differently. The court summons technical judges to whom technical questions are submitted and who can intelligently pass upon the issues without blindly groping among testimony upon matters wholly out of their ken. How long shall we continue to blunder along without the aid of unpartisan and authoritative scientific assistance in the administration of justice, no one knows; but all fair persons not conventionalized by provincial legal habits of mind ought, I should think, to unite to effect some such advance." (See Parke-Davis & Co., *vs.* H. K. Mulford Co. Circuit Court, Southern District of New York, April 28, 1911—189 Federal Reporter, 95.)

Even under the new rules, it will not be difficult to drag on a case by presenting an unrestricted amount of testimony taken before an incompetent examiner, and by calculating every step so as to tire out your opponent and so as to induce the judge in doubt and error, by swamping him with endless contradictory expert testimony calculated to befog the issue instead of making it clear. Such tactics are relatively easy for the litigant who, for that purpose, can afford to pay accommodating experts and skillful lawyers. Even if at the end, the judge, after laborious and conscientious efforts, masters the technicalities of the case and reaches a good decision, much needless time has been wasted. All this might easily be avoided, and judges might be saved the trouble and responsibility of going in every single case through a different scientific or technical training, if their intervention could be limited to what they are more competent for, namely, to determine what claims have been infringed and in how far this infringement entitles the patentee to damages.

That such a method of settling patent suits is quite practical, is shown by the example of Germany. In that country, patents are allowed after preliminary examination, just as here; but, after the patent is granted, it can be attacked for annulment or revocation before a competent court in the Patent office; so that any party who is sued for infringement of a patent which he thinks is invalid, can avoid temporarily the adjudication of the infringement issue by starting an annulment or revoca-

tion suit. In the meantime, the courts in which infringement cases are examined have to take the patent as it stands, and it is only left to them to interpret the scope of the claims, and to what extent these claims have been infringed.

This relieves the equity court of all the complicated questions of validity or non-validity of a patent, and puts this whole matter in the hand of a properly constituted court of experts who can handle this subject with incomparably less hesitation, or delay. Besides this, the whole system of practice in the German Patent Office tends towards systematic elimination of invalid patents. After an examiner has decided upon preliminary allowance of a patent, the claims and specifications are open for public inspection, and for a period of two months, anybody whosever can file arguments against the final grant of the patent. In this way, the nation does not confer patent privileges too lightly and has, furthermore, the benefit of the free advice of any experts in the art, who may advance good reasons for non-allowance of the claims, of which the examiner was not aware when he rendered his first decision. These opposition proceedings give added thoroughness to the work of the examiners. They are relatively inexpensive and do not necessitate the intervention of law counsel. Sometimes they delay the issue of a patent, if there is any good reason for doing so. On the other hand, a patent that has successfully withstood vigorous opposition proceedings is very much strengthened thereby; this, in itself, is a very valuable compensation for any delays to which the patentee may have been subjected. In other words, by that system, a good patent becomes stronger, while a defective patent application is easily weeded out. A similar system of public opposition exists here in the United States in relation to the granting of Trade-Mark rights, and seems sufficiently practical that it could be extended to our methods of allowing patents.

Such a sifting process, first by the examiner, then by opposition proceedings, sometimes by annulment or revocation proceedings for wrongly issued patents, involves no serious difficulties nor great loss of time if carried out by courts of experts. Thanks to such a system, the work of a judge who acts on an infringement case, gains considerably in dignity and is, at the same time, enormously shortened and simplified. (See Wertheimer, *The German Patent System*, *THIS JOURNAL*, 4, 464.

The German system throws the burden of technicalities and expert knowledge on the Patent Office, or the Courts connected therewith. Nothing would be easier than to introduce a somewhat similar system in our country.

All officers of our Patent Office, high or low, should be made independent of any political favoritism; they should be better paid, with more opportunity for promotion, according to merit; their work should be made simpler by an improved office equipment and increased facilities for a thorough search; furthermore, our unnecessarily complicated and expensive methods of interference proceedings should be simplified.

With these reforms, there is no doubt that we can organize right in the Patent Office, a competent court, supplemented by the court of appeals of the District of Columbia, for deciding, in a very expedient way, all questions of validity of patents.

This court of appeals, because it is situated right in Washington, would have easy and immediate access to all the records of the Patent Office; by this fact alone, it would have superior opportunities for prompt and efficient work.

During the late years, Germany has been trying to broaden its patent laws more and more towards the principles set forth in the American Constitution. For instance, it has practically eliminated the system of compulsory licenses except in some rare instances where public welfare is involved. If only we could borrow some of the more efficient methods with which

the German patent law is administered, and enforced, we might succeed in making an American patent *real* property for poor and rich alike, instead of a pretext for expensive and endless litigation with all the advantages it gives to the richer litigant, to the detriment of the consumer who, in the end, pays the bill.

At least some of these facts seem to have been very well recognized in the masterly report of Hon. William A. Oldfield, chairman of the House Committee on Patents. (See report No. 1161, on H. R. 23,417, Aug. 8, 1912.)

Unfortunately, his proposed Oldfield Bill (H. R. No. 23,417), with a regrettable lack of consistency, neglects utterly the paramount issues, and busies itself with secondary regulations which, if carried out, will practically put a penalty on patented articles.

The new provisions of the Oldfield Bill aim at curtailing the power of patents in the hands of trusts or large corporations; but, in doing so, new provisions are introduced which will create endless new opportunities for protracted litigation.

The Oldfield Bill overlooks the axiom that whatever increases the expense or delays of litigation is a very potent weapon in the hands of large corporations, which they can hurl against the poor litigant who stands in their way.

The saddest thing of all is that the new Oldfield Bill tries to abrogate the hitherto accepted principle established by our Constitution, that a patentee has the right to license or sell his patent on whatever terms he pleases. It has been feared that this principle, if carried too far, might become a dodge for avoiding Anti-trust Laws. Since the decision of the famous, but harmless, Dick case, the most hysterical exaggerations have been published on this subject. Fortunately, since then, the recent and unanimous decision of the United States Supreme Court in the "bath tub trust" case, Nov. 18, 1912, does away with all these redundant arguments and settles, beyond doubt, the principle that, patent or no patent, unlawful combinations in restraint of trade can be stopped by the Sherman Law.

The Oldfield Bill, in its eagerness to avoid any hesitation on this subject, goes one step further, and unfortunately one step too far. It puts so many restrictions on the sale of a patent article, or on a patent license, that it may become a positive disadvantage to transact business by means of patents.

Examined in last analysis, it threatens a business based on patented processes or patented articles, with penalties which unpatented articles thus far are not subjected to. It takes the proposed patent law as a pretext for saddling a patented article with restrictions which have not heretofore been formulated for non-patented goods.

This unexpected paradox, promoted by the Oldfield Bill, is distinctly in opposition to the rights of intellectual property conveyed by the words and the spirit of the Constitution, and if the Oldfield Bill becomes an effective law, it will be the saddest blow ever given to our patent system. It will do comparatively little harm to large business interests, because for them there are many ways of circumventing its provisions; on the other hand, it will cause great discouragement to smaller enterprises who, until now, have held the hope of matching inventive genius and initiative against the money power of big organizations. Make a large corporation respect the patents of a small concern, or of an individual, and you reduce at once any advantage of size or money power, and at the same time, you encourage the most beneficial form of competition—competition based on improvements. But to introduce curtailing restrictions for the licensing or selling of patented articles or patented processes to which non-patented articles are not subjected to, means simply obliterating the value of patents while needlessly increasing still further the opportunities of endless and ruinous litigation and chicanery.

Another unfortunate miscarriage of purpose in the Oldfield Bill is its provision against so-called wilful "suppression" or

"non-use" of patents. It does not take into consideration that in numerous instances a patentee or an assignee possesses a series of so called alternative patents, which can be used to bring about identical or similar technical results by modified means. Among such alternate patents, the best or the most suitable is used, absolutely irrespective of any other reason or intention to suppress their use. Yet without the exclusive possession of every one of these patents, the invention would not sufficiently protect against competitors, and the field would be so much reduced as not to make it worth while to put one's best energies to the development of the invention. In most cases, it would become a material impossibility for a small concern to maintain the exclusive ownership of its patents, if it had to go to the enormous expense of working simultaneously all its "alternate" patents; by omitting this expensive technicality, it would be exposed to the risk of being compelled by its competitors to grant a compulsory license; this would practically annihilate the advantage of exclusive ownership as expressed by the Constitution. There again large concerns would be at an overwhelming advantage because they can, at an expense relatively small for them, equip the necessary appliances for remaining within the technical provisions of the law. In the meantime, they could easily harass their financially weaker competitors by exacting from them compulsory licenses which would break up the only prospects of successful competition which the smaller concern might have possessed, until then, in its patents.

In other words, the Oldfield Bill is aiming at the petty side of the situation and, in doing so, has unwittingly picked out a vital spot of our patent system. It reminds one of the man who set his barn afire in order to drive out a hornets' nest.

I have no doubt that this bill has been framed with the best intentions for the interests of the country. Unfortunately, the framers of this bill do not foresee the far-reaching and dangerous effects of its provisions.

The average man, even the average legislator, has a rather one-sided conception of patents or inventions. Most people's idea of a patent does not go far beyond some simple mechanical device, like a patented mole-trap, a safety razor, an alarm clock or other similar invention, more or less easy to understand after the apparently simple mechanical principles have once been explained. Then everything seems so simple and easy to them that their limited imagination cannot conceive how even these apparently simple devices have frequently cost incredible efforts and immense amounts of money before their advantages become available to the public.

This attitude of mind develops, naturally, the belief that a patentee has a "soft snap," the result of a lucky idea, in about the same way as a lucky prospector strikes a rich gold mine, or a lucky ticket draws the grand prize in a lottery.

Precisely on this account, it becomes difficult to explain to such people the rights and purposes of intellectual property; it is still more difficult to convince them that the nation is greatly benefited by liberal patent laws.

When it comes to chemical patents, the ignorance of the average public is amusing if not pathetic. Since we have heard a New York alderman in an official address of welcome to the members of the International Congress of Chemistry speak as if they were druggists or pharmacists, we must no longer be astonished if the average Congressman or Senator refers to a chemical patent as a synonym of "patent medicine."

But it is even difficult for the better prepared legislators to understand how some chemical inventions have brought about the most far-reaching developments, not only in other industries and arts, but in civilization itself. For instance, it is not so obvious to them how processes for fixing the nitrogen of the air, or extracting soluble potassium salts from rocks, enable us to make food supplies independent from the restricted potash

mines in Germany or the nitrate deposits in Chili. Such inventions are no more nor less than means for preventing possible starvation of our race. Do they realize that the development of the automobile, with all that it directly and indirectly implies, was entirely dependent on Goodyear's vulcanizing process of rubber? Shall we remind them of the fact that without the invention of explosives like dynamite, gigantic engineering enterprises, the Panama Canal, blasting of rock for the excavation of our cities, mining for ores, tunneling and grading of railroads, would be impossible? How could we expect even the most perfected modern printing presses to distribute to every citizen, rich or poor, young or old, that knowledge and culture which means better citizenship, better opportunities for happiness and development of our race, if it were not for the inexpensive and abundant supply of paper furnished by the cellulose processes. The Greeks, the Romans and even the Middle Ages had their sages, their poets; yet those were the times of slavery and oppression, because knowledge was in the reach of only such a limited number that it was possible for tyrants to throttle its diffusion by sending the few advanced thinkers to the gallows or burning them alive. For the same reason, scarcity of books, the destruction of the library of Alexandria was a calamity for the intellectual development of mankind. Our abundant supply of cellulose makes a repetition of such conditions an utter impossibility.

Then again, where would we find our supplies of steel, the main raw material for modern engineering, if the Bessemer, the Thomas-Gilchrist and others had not invented their processes? How about the marvelous syntheses of products derived from coal tar, which have literally created the most astounding series of new substances, which have revolutionized therapeutics, surgery, hygiene, and are finding daily new applications in the most varied arts and in general technology?

At a time when all countries are confronted with that critical question of the increased cost of living, it may be interesting to point out that just those industries where invention and patents have played the smallest rôle, are also those where the increase of price is most burdensome, while those commodities where patented inventions have had the fullest influence, have, on the contrary, decreased in price and, in some instances, to an astonishing degree.

For instance, the price of sulfuric acid is about fifteen times less than it was in 1807, and about one-half of that of 1870. The price of soda ash is about one-sixth of what it was in 1823, and about one-half of the price in 1860. Nitric acid sells for less than one-half the price of 1861. Glycerine sells for about one-eighth of the price of 1855. Chloride of lime in 1800 sold for 30 cents a pound, in 1870 for about 2 cents per pound, today for about 1 cent a pound. Any chemist knows that every one of these products is used directly and indirectly in the most ramified channels of our arts and industries, but the layman does not know that cheap soda means cheap soap, cheap paper, cheap glass, etc., that cheap sulfuric acid means cheap fertilizers, better crops, cheaper corn, cheaper wheat, and so forth.

Let me point out that the decrease in price of these materials is even considerably greater than the bare comparison of figures indicates, if we take in consideration that the purchasing value of money has considerably decreased, while the cost of labor has enormously increased.

Nor are these examples merely confined to chemical products. The reduction in price for articles where patents have played an important rôle, is just as evident in steel products, tools, machinery, etc.

Compare these lower prices with the vastly increased cost of rents, clothing, food-stuffs, and many agricultural products, where patents have played a less preponderant rôle. If you will carry your analysis still further, you will find that in such branches of trade where patented inventions have had little

or no importance, for instance, cattle raising, prices have soared highest. On the other hand, for such agricultural products where patented machinery could be used to best advantage, like wheat and corn, the increase of price has been relatively small. Then again, garden vegetables, potatoes, etc., where the use of patented agricultural machinery is less available, show an enormous increase in price.

You may object that the price of shoes has gone up, but here again, the increase is entirely due to the greatly advanced price of hides, and were it not for the perfected shoe-making machinery and for the better and cheaper chemical tanning methods, all due to patents, the cost of our shoes would be so high that they might again become an article of luxury, available only for the well-to-do.

The present price of clothing is high enough as it is; nevertheless, it would still be much higher but for the patented machinery for spinning and weaving, the patented chemical processes of bleaching, dyeing, mercerizing, etc.

I should not omit to mention our vastly improved and cheapened methods of transportation, of production of power and light, all developed and perfected on an interwoven system of patents; I could explain the far-reaching influence thereof on civilization, culture, on the happiness and security of life of the individual citizen; but even, then, I might not convince the pessimist or the scoffer who sees only the hole in a doughnut and stubbornly persists in ignoring the doughnut itself.

The history of almost every invention which we are utilizing now, unconsciously, every day, is an epic by itself, the details of which are known only by the few pioneers who gave the best they had to give, who helped with their brains, with their money, and talent of organization: some with their very lives.

The often repeated statement has been made: "An inventor cannot help inventing, whether you give him a reward or not." Then again, some others say: "Necessity is the mother of invention."

The most apparent fact is that the man who receives an ample income from his father, or some other privileged source, is less prompted to distinguish himself by arduous creative work on inventions, than the poor but intelligent man who sees in invention a means of making himself financially free and independent, as well as giving an outlet to his inventive abilities.

Whoever has followed intimately the development of some chemical processes, knows very well that whether "the inventor cannot help inventing," or whatever may be the incentive to invention, most of these important inventions could never have been carried out, or could never have been brought to the point where they became of public benefit, but for the intelligent use of vast sums of money. Too few people have a conception of the immense sacrifices, of the serious money risks, involved in the development of some patents. Many chemical inventions, used now currently and open to the public at large, have cost millions before they were brought into practical shape, or before the public was educated to their advantages. Can any one expect that such expenses, such efforts, such risks, would be undertaken, unless there was the possibility of at least some chance of recouping by a temporary patent protection?

Let us take, for instance, those large German chemical companies which employ hundreds of chemists and engineers, engaged exclusively in research work; to them, we owe the development of many processes which have had an untold beneficial influence in many directions on the economics of our daily life, even on civilization itself. They employ large aggregations of capital, reaching into many millions. The dividends of some of these companies may appear large to the superficial observer. Yet if you look more closely into it, you will find that these very companies were founded long ago, some of them over half a century or more, that the large capital which they employ has never been "watered," that although

they have had the benefit of the devoted cooperation of an endless number of distinguished men, stars of first magnitude in their profession, the net returns on their invested capital, at the end of half a century of brilliant intellectual pioneer work, is relatively small, even if the dividends seem large. In fact, the net returns are decidedly lower than that of many American enterprises not over fifteen years old, and where progressive technical leadership was entirely lacking, but where tariff privileges and agglomeration of competing concerns, into a trust, insured a splendidly paying monopoly, notwithstanding the reckless financiering of their promoters.

If you will further investigate the history of those German chemical concerns which have become leaders of the industrial world by nothing but their intellectual pioneership, you will find that notwithstanding all the patents on which they have to rely, the expenses involved in research work and pioneership swallow up, to a large extent, the profits realized in some of the established branches. But with true scientific spirit, their far-sighted directors were willing to sacrifice a very considerable part of their earnings, in their search for improvements and development of new ideas; they have set a magnificent example in the only competition beneficial to the public, *competition by improvement*.

One of our wealthiest retired multi-millionaire manufacturers, not so long ago, speaking about his money successes, gave the following advice: "Never be a pioneer; it does not pay. Let the other man do the pioneering, and then after he has shown what can be done, do it bigger and more quickly; but let the other man take the time and the risk to show you how to do it." To anyone who advances the statement that an inventor "cannot help inventing," I desire to ask whether an inventor will do much inventing, if in order to carry on his research work, or to develop his invention, he has to spend hundreds of thousands nay sometimes millions of dollars, but does not possess them, and nobody is willing to take the risk to furnish the money unless there is a fair chance for his backers of obtaining some compensation by a temporary patent protection? Those who know the large sums of money which have been swallowed up by the research and development work connected with the artificial production of nitrates; with the Solvay soda process; the development of the steam turbine; electric light, electric traction, and numerous other inventions of far-reaching magnitude, will know what I mean.

Just on this account, it is highly unreasonable of the Oldfield Bill to try to make a distinction between the inventor in whose name the patent is drawn, and the party who runs the risks in enabling the inventor to make the invention available to the public; any such legislation simply tends to discourage those who, at considerable risk, furnish the capital and the talent to develop an invention into a commercial possibility, and who thereby bring it into real public service.

Now and then, I have perceived that some of my fellow chemists who, although highly trained, have never created anything of technical value, and whose experience with matters of practical life frequently extends not beyond the confines of their lecture-room or their laboratory, do not seem to grasp fully the immense distance that lies between the initial conception of an invention, or its study in the laboratory, and the overwhelming amount of careful work and money risks connected with its development on a commercial scale, until it has safely reached the point where the public can avail itself of the invention.

I wish to cite, for instance, the famous Solvay process, which gives us cheap, excellent and abundant soda, an article of prominent importance in the wheels of our civilization. This process was known and described more than a dozen times, and had even been tried repeatedly at considerable loss, on a commercial scale, many years before Solvay tied his genius to this difficult

problem and developed, from an unreliable laboratory reaction, a process of great industrial importance, then, with a staff of able collaborators, and the employment of large amounts of cash, he overcame, by and by, the technical drawbacks which had caused the failure of all of his predecessors.

Hundreds of similar examples could be cited. Whoever has been intimately acquainted with the commercial development of some of the most successful inventions, knows quite well the risks, dangers of failure, which have accompanied the herculean task of development and educational work. It is a well established fact that the great majority of new enterprises fail; that few succeed.

The educational effect due to the introduction of patented inventions is of immense benefit to the public, although this fact is not very apparent to most people. In many instances, the owner of a patent frequently has to go to extreme sacrifices before he succeeds in convincing the public of the merits of his invention; in fact, the public stubbornly refuses to benefit by an improvement to which it has not been fully educated.

The practical value of cash registers became obvious only after a most thorough and very expensive educational campaign.

The metric system is just as useful as the cash register; it was invented long ago and systematized in all its details during the first French republic. Nevertheless, to-day, there are still two large commercial countries, the United States and England, which have not yet been educated to its merits; if the metric system had been patented, like the "cash register," somebody, during the seventeen years of the patent monopoly, would have undertaken the money risk and arduous task of thoroughly explaining the advantages of the metric system to our conservative citizens, and we would have ceased long ago to submit to the burden of waste of time and money caused by our antiquated, cumbersome system of weights and measures.

It has been stated, with much reason, that the best way to postpone the benefits of an invention, is to allow public use of a patent, because then nobody takes the risk of starting an educational campaign or of developing the invention, which after all means pulling the chestnuts out of the fire for the benefit of others.

Entirely new industrial enterprises are not easily started on inventions which are not patented, unless some other method is available for insuring some kind of a monopoly; for instance, by maintaining secrecy or by acquiring special skill, or by controlling the raw material, or by tying the market, or in other instances where the initial outlay for a plant requires a capital so large as to exclude others.

Moreover, if you scrutinize those industries where secrecy of methods, instead of published patents, is the prevailing tendency, you will find that the secret-process-industries are precisely those which have least progress to record, and where high prices rule.

Whoever desires to get posted on the modern literature pertaining to any industrial chemical process, will find that available text-books are many years behind in information as far as novelty and accuracy are concerned; for this reason alone, it is absolutely indispensable to get acquainted with all recent patent literature.

Were it not for the compensation expected from patent rights, most of this information would be carefully kept secret, or if it were divulged at all, this would mostly occur by accident. Every newly published patent sets to work the thinking cells of numerous inventors, who are not slow to suggest further possible improvements. Every patent of some importance is rapidly followed by a succession of other patents conceived by other inventors, who were inspired by their predecessors, and so the work of progress goes on unceasingly and at a quickened pace.

In the age of the alchemists, there were no patents; inventions

and discoveries were jealously guarded and buried with their originators, and the world and its inhabitants remained very much what they were with most rights and comforts in the possession of those in power, and very little chance of improvement for the non-privileged classes.

The public should be educated in these truisms. Unfortunately, the education of the public has been directed in the opposite way since patent infringers have utilized the daily press after the late decision of the Supreme Court in the Dick case, to start a campaign for urging our well meaning but ill-prepared legislators towards patent reform, which will give still broader scope to our modern buccaners. This reminds us of the man who, after stealing a stranger's pocketbook, kept on shouting "stop, thief," so as to distract the attention from himself.

Two ways are open for our legislators:

One way is to try "to hit the trusts" by mutilating the best there is in our patent system, which has been such a potent factor in the development of our country; to chill the best incentive for private enterprise; to stunt that kind of competition most beneficial to the public, competition by improvement, incomparably better in this respect for stimulating industry, science and progress, than protective tariff privileges which, in many instances, have worked in the opposite direction.

The other way is not to put dangerous restrictions on the patent rights defined by our constitution. If there has been any fear that such patent rights might be abused for evading the provisions of the anti-trust laws, these apprehensions have vanished by the clear unequivocal decision of the Supreme Court in the Bath Tub Case.

But there is urgent need of reform in our patent system by simplifying procedure in the Patent Office as well as in the courts, by insuring better, quicker and less expensive means for adjudicating the title and validity of patents. Only such a reform will bring about that big or small, poor or rich alike may be stimulated by the advantages of our patent system, instead of making a patent an expensive but powerful instrument, available only to the wealthy.

Whatever simplifies and lessens the cost of the administration of our otherwise excellent fundamental patent law, gives the enterprising man with small means a better chance of competition by inventive progress and merit against ponderous aggregations of capital. By such reform, which insures such healthy competition, the nation is sure to be benefited.

In all above considerations, my remarks were principally inspired from the standpoint of chemical patents, not alone because this very important class of patents is least understood by the average public and the legislator, but because chemical process patents are also those which are most difficult to protect from infringers.

THE PERMANENT FIREPROOFING OF COTTON GOODS¹

By WILLIAM HENRY PERKIN

When I had the honor of being asked to deliver one of the General Lectures, I had no choice but to accept, and yet it was at once evident to me that I should experience very great difficulty in finding a subject suitable to this occasion and interesting to the brilliant and distinguished audience which I see before me this afternoon.

This difficulty is due to the fact that, while I have always taken an interest in industrial questions and have repeatedly investigated industrial problems from the scientific point of view, my researches have, for the most part, lain in the path of pure Science, and any practical application of my researches to the Chemical and Allied Industries, I have had to leave to others.

Among the problems of technical interest which I have worked

¹ General Lecture by Dr. William Henry Perkin, F.R.S., Professor of Chemistry, Manchester, England. Eighth International Congress of Applied Chemistry, New York, September, 1912.

at during many years are the manufacture of artificial camphor, of "synthetic" rubber and more particularly the permanent fireproofing of cotton goods and other inflammable materials. In considering these subjects, I concluded that the problem of the manufacture of artificial camphor was too technical to be generally interesting and my friend—Professor Duisberg—wishes to introduce the subject of "synthetic" rubber into his General Lecture so there remained the subject of permanent fireproofing, which, in many respects, is perhaps as interesting and important and as difficult of accomplishment as the other problems I have mentioned. The problem of the prevention of fire has always been one of the most pressing and, at the same time, one of the most difficult and perplexing with which mankind has had to deal. In very early times wooden houses caught fire and were burnt down and it is said that the Romans attempted to render wood fireproof by dipping it in a bath made of vinegar and powdered clay.

This treatment, so strongly reminiscent of processes employed many years afterwards, would, no doubt, be effective in rendering the wood less liable to inflame, but it can hardly have had wide application because vinegar, in those days, was not easily obtained in quantity and was consequently an expensive substance. I have made a search in a number of old books with the object of discovering some other of the actual methods used in early times in connection with fireproofing, and the first pamphlet on the subject which I have been able to find, dates from 1638 when Nikolaus Sabbattini published a remarkable paper in which he discussed the need of reform in the administration and construction of the theatres in Italy and pointed out the danger, which is always present, of fire breaking out on the stage, not only owing to the inflammable nature of the wood employed in the construction of the theatre and for the decorations and scenery but also on account of the inflammability of the cotton material used in the scenery and for the dresses of the players.

He recommends, as a safeguard, that the color used in painting the theatre and scenery should be mixed with clay and gypsum but says nothing about the fireproofing of the dresses.

At a considerably later date—in 1735—Wild suggested a mixture of alum, borax and sulfuric acid for the same purpose and, in 1740, Fagot, in a paper read before the Academy in Stockholm, recommended a mixture of alum and green vitriol whereas, in the Dictionnaire de l'Industrie published in the year 1786, there is a paragraph in which it is stated that a mixture of alum, green vitriol and salt is effective in making wood and other material fireproof.

After the disastrous fire in Munich on the 14th of January, 1823, which completely destroyed the Hof and National Theatre, a large number of experiments were made with the result that the wood used in the construction of the roof and other parts of the new theatre, was painted with several coats of sodium silicate and chalk.

A coating of this kind lasts for many years and, although it does not render the wood absolutely non-inflammable, it has at least this value that the incipient fire, which as a rule begins in quite a small way, meets with resistance at the outset, progresses but slowly and is easily extinguished.

At a somewhat later date, it was discovered that wood saturated with other salts such as, for example, copper sulfate or ammonium phosphate, acquires the property of resisting flame, but of all the salts, zinc chloride seems to be the most efficient for this purpose.

In the first place, zinc chloride has great affinity for, and, therefore, attaches itself readily to, woody fibre, and fibres of all kinds and material saturated with a solution of this salt and then dried are practically non-inflammable. This salt has also this valuable property that it is a powerful antiseptic and therefore very suitable for fireproofing the wood used in the construction of hospitals and other public institutions of a similar nature.

But I do not propose to address you this afternoon at any length on the subject of the fireproofing of wood and other building materials, a subject on which I have made comparatively few experiments and of which I, therefore, have little practical knowledge.

What I wish to discuss, and I hope that the subject will prove interesting to you all, is the problem of the permanent fireproofing of wearing materials and especially of cotton and cotton goods and by permanent fireproofing I mean protection which is not removed when the materials are subjected to the ordinary domestic wash.

Many disastrous accidents are on record which have been brought about by clothing catching fire: sometimes it is the case of a child whose garments have come in contact with a spark or lighted match and sometimes disasters of much greater magnitude have resulted from the ignition of costumes made of tow or other inflammable material on the occasion of charity entertainments or fancy dress balls.

It has long been recognized that impregnation with certain salts very much reduces and indeed may entirely destroy the liability of cotton goods to inflame and, of these fireproofing agents, I may perhaps be allowed to refer to a few only of the better known and more efficient. If a garment, after washing in the ordinary way, is rinsed in a solution containing alum or is starched with a starch containing a proportion of alum, the material, after drying, shows a marked reluctance to ignite, but this treatment has many draw-backs. In the first place it makes the material very dusty, and secondly the fireproofing is only of a temporary nature since it is at once removed by contact with water and the process must, therefore, be repeated every time the goods are washed. I can easily demonstrate this and, in these and all my other experiments, I purposely take only very narrow strips in order that any smoke produced may not cause inconvenience in this Hall. Another solution which has been strongly recommended for the same purpose is made up with 3 parts of ammonium phosphate, 2 parts of ammonium chloride and 1 part of ammonium sulfate in about 40 parts of water. If the material, after washing, is impregnated with this solution and dried, or if it is starched with starch made with the solution instead of with water, the dry material ignites only with difficulty, and, as it does not dust and is not prejudicially affected in any other way, this process has been used with advantage not only in connection with wearing material but also for the fireproofing of lace curtains and other inflammable decorations. But in this case also, the fireproofing agents employed are all soluble in water and one washing is sufficient to remove them entirely, leaving the goods at least as inflammable as before. The process must, therefore, be repeated every time the goods are washed and this means expense which, in the long run, becomes considerable.

But a much more serious drawback to processes of this kind is the trouble they entail since, in order to fireproof the garment, the washerwoman must have alongside the ordinary wash tub a second tub containing the fireproofing solution and this complication, added to the expense of the salts, has been shown to be so serious that processes of this kind are quite impracticable, especially in the homes of the poor. Again, unless the materials or garments, after washing, have been dried before immersion in the fireproofing solution, this solution cannot be kept uniform since each garment being wet when put in leaves the solution weaker than before and therefore of less protective value. To dry each garment between the washing and the fireproofing entails so much trouble and labor and expense that it would obviously prevent any general adoption of the practice. Although the substances I have mentioned, and the salts of ammonium in particular, possess, in a high degree, the property of rendering material fireproof, there is one substance which confers the property of resisting fire to cotton goods in such a

remarkable degree that it has long attracted attention and must be specially mentioned, and that is sodium tungstate.

A piece of muslin soaked in a weak solution of sodium tungstate and then dried is practically non-inflammable but unfortunately this salt is again so excessively soluble in water that a mere rinsing in clean water is sufficient to remove it completely and the fireproofing is lost. And this applies not only to sodium tungstate but also to all the other salts which have, from time to time, been recommended for fireproofing purposes; the result is not permanent because the proofing is at once removed when the goods are washed in the ordinary way.

The problem on which I was engaged for several years and which has now been successfully solved, in a very simple manner, was that of attempting to discover some process which not only made the goods non-inflammable but also *permanently* non-inflammable, and the researches on this subject were originally started in connection with flannelette, a material very largely and widely used for clothing especially by the poorer classes, and one of the most, if not the most, inflammable of all cotton goods.

Flannelette may be briefly described as a kind of calico, the surface of one or both sides of which has been "carded" or "raised" into a nap, the result being that the surface of the calico becomes covered with a fluff of minute fibres somewhat resembling a thin layer of cotton wool. This effect is produced by subjecting the surface of the calico to the action of a series of revolving rollers covered with a vast number of small pieces of sharp steel wire, which tear up the surface, and the material is passed over these rollers over and over again until the required amount of nap has been raised. The result of this superficial covering of nap is—as everybody who has handled flannelette will know—a warm, pleasant and cosy feel and this is, no doubt, due to a covering of air being imprisoned by the minute fibres, thus producing a layer which acts as a non-conductor much in the same way as in the case of flannel.

In the first two samples in the little book which you each received as you entered the Hall are calico and flannelette and you will notice at once the great difference in the feel between the comparatively hard flat surface of the calico and the raised surface of the flannelette.

Flannelette is indeed little, if at all, inferior to flannel as a non-conducting material, and as it is very cheap and does not shrink in the wash, it has become very popular and is manufactured in enormous quantities and almost universally used for the clothing of children, especially in the homes of the poorer classes.

But it was not long before its increasing use showed unmistakably that it has one terrible drawback—the nap, which is its peculiar feature, makes it highly inflammable and much more so than the calico from which it was manufactured.

Flannelette is, in fact, as I have already said, very much like calico on the surface of which a thin layer of cotton wool has been spread and this layer is, of course, highly inflammable.

I can easily demonstrate the difference in the inflammability of calico and flannelette by applying a light to strips of each when it will be seen that while calico burns in the ordinary way, in the case of flannelette, the flame flashes over the whole surface of the fluffy cotton layer and travels with extraordinary rapidity.

It is, of course, this property which makes flannelette one of the most dangerous of materials for clothing purposes. The alarming frequency of deaths by burning due to the wearing of flannelette became common knowledge, the coroners all over Great Britain repeatedly called attention to the matter and by degrees the agitation against its use for clothing became so persistent that the Coroners' Committee of the Home Office was directed to inquire into the matter.

The Committee recognized that while, to quote the words of their Report, "We think the common opinion attributing to

it (flannelette) a large share of the blame (of burning accidents) is not far wrong," that it was impossible to prohibit its use without causing great hardship especially to the poor. Several years before this inquiry was held, one of the largest firms of flannelette manufacturers in Manchester, Messrs. Whipp Bros. and Tod, becoming alarmed at the frequent occurrence of fatal burning accidents and fearing lest these might lead to the prohibition of the sale of the material, came to me and asked whether I would undertake a series of experiments with the object of endeavoring to find a remedy for this state of things and, after looking carefully into the matter, I consented to do what I could. That the problem was a difficult one from many points of view will be readily understood if I briefly state the conditions which had to be kept constantly in mind while the experiments were being carried on. A process to be successful must, in the first place, not damage the feel or durability of the cloth or cause it to go damp as so many chemicals do, and it must not make it dusty. It must not affect the colors or the design woven into the cloth or dyed or printed upon it; nothing (such as arsenic, antimony, or lead) of a poisonous nature or in any way deleterious to the skin may be used and the fireproofing must be permanent, that is to say, it must not be removed even in the case of a garment which may possibly be washed 50 times or more. Furthermore, in order that it may have a wide application, the process must be cheap. What was really to be aimed at was to treat the flannelette in such a way that it acquired practically the properties of wool which, for all ordinary purposes, may be taken as the standard of a safe material. Apart from the other conditions which I have laid down, when one considers the vigor with which the ordinary washerwoman scrubs garments with soap, not infrequently with the assistance of the scrubbing brush, and takes into account the wonderful mechanical appliances now so largely used for washing clothes with the least expenditure of time, it will not be thought surprising that the discovery of a process of fireproofing sufficiently permanent to resist all these conditions seemed to me at first to be almost an impossibility.

In describing the course of the research, I may perhaps be allowed to give a brief sketch of the development of the subject and to outline the reasoning which led to the institution of the various experiments. Some idea of the difficulty of the subject will be gathered when I say that Mr. Samuel Bradbury, who so ably assisted me in the work and has kept a record of each experiment, tells me that upwards of 10,000 separate burning tests were made before the solution of the problem was reached. Besides these, a great number of further experiments have since been made to see whether an even cheaper process than that which has now been in commercial use for nearly 10 years could be discovered.

I suppose that every one would agree that, at the outset of the experiments, the condition which seemed most difficult of realization was that of finding a substance which not only fireproofs but which during the process becomes so permanently fixed that it will prove to be absolutely resistant to washing with soap and water or mechanical rubbing. Obviously the substance which is to fulfill these conditions must, in the first place, be insoluble in water and secondly in order that it is not liable to be removed by mechanical rubbing and does not render the cloth dusty, it must be fixed in the fibre and not be merely on the surface. I have already explained that when calico is dipped in a dilute solution of sodium tungstate, and then dried the material possesses, in a remarkable degree, the property of resisting flame and then again alum has often been recommended for the same purpose. Now when solutions of sodium tungstate and alum are mixed, an insoluble aluminum tungstate is produced and it is clear that, if this insoluble salt could be fixed in the fibre, the material would certainly be fireproofed. It furthermore seemed reasonable to suppose that, as the salt is insoluble in water, it would remain in the fibre even after several washings and

therefore that permanent fireproofing might be achieved in this manner.

A piece of flannelette was, therefore, soaked in sodium tungstate and, after passing through rollers, to remove the excess of the solution, left for a considerable time in a solution of alum. It was then squeezed, dried and was passed through the same process again with the result that the material became almost as fire-resistant as asbestos. When, however, the piece was thoroughly washed with soap and water, it was most disappointing to find that the greater part of the fireproofing was removed during the first washing and after several washings, the material was little better than the original flannelette.

While this unexpected result was being investigated, it was noticed that aluminum tungstate is soluble in acetic acid and is reprecipitated when the acetic acid is removed by evaporation or by the action of steam and as the precipitate formed seemed granular in appearance, it was thought that this process, if applied to the flannelette, might yield a better result than the process of double decomposition had done. Accordingly, a solution was made up of sodium tungstate, aluminum sulfate and enough acetic acid to dissolve the precipitate, the flannelette was thoroughly soaked in this solution, dried and then placed in an ordinary steamer and subjected to the action of steam until the odor of acetic acid could no longer be detected.

The material was, of course, non-inflammable and when it was washed, it was found that this property was distinctly more resistant to soap and water than was the case in the first experiment, but after several vigorous washings almost every trace of the fireproofing had disappeared. These negative results seemed therefore to indicate that aluminum tungstate was not suitable for the purpose of permanent fireproofing. On the other hand, the failure of this salt was possibly due to some peculiarities in its specific properties and was not considered valid evidence that other insoluble tungstates might not combine more completely with the fibre and thus resist removal by washing.

A careful examination of the tungstates was, therefore, made and only such insoluble salts selected for experiment which, like aluminum tungstate, are colorless since it is obvious that a fireproofing agent to be of any use must be capable of application to white cloth without staining it. Several hundred pieces of flannelette were treated under the most varied conditions with all sorts of combinations which it was known would precipitate insoluble tungstates in the fibre but in no case was a satisfactory result achieved.

However, a fact was noticed which afterwards proved to be of value and it was this: that, of all the salts, the tungstates of zinc and tin seemed to offer the most resistance to washing with soap and water. Thus, when the material had been thoroughly saturated with a solution made up of sodium tungstate, zinc sulfate and enough acetic acid to prevent the precipitation of the zinc tungstate, and the goods after drying were thoroughly steamed, the fireproofing was certainly fixed to some extent since it required several washings before the material burnt at all freely. But no amount of variation of the conditions produced a really good result and this combination had, therefore, to be abandoned. Since the tungstate proved to be unsuitable to the exacting conditions of the problem, a general examination of almost every variety of salt, including ferrocyanides, aluminates, arsenates, antimonates, zincates and plumbates, was made. Many of these could not be employed in connection with wearing apparel in any case because of their poisonous nature but it was thought that this general examination, which lasted several months, might yield some indication of the type of salt likely to prove resistant to soap and water, if, indeed, such type of salt existed at all. And as a matter of fact these experiments did prove to be most valuable, because when the results were all tabulated, the generalization gradually became apparent

that certain soluble salts, such as aluminates, antimonates, zincates, and plumbates, in which the oxide of the metal functions as an acid, yielded precipitates especially with zinc and tin salts which exhibited much greater resistance to washing than the commoner insoluble salts, such as barium sulfate or magnesium phosphate. This generalization ultimately led to a very careful examination of the salts of tin because, as is well known, the oxides of tin dissolve in alkalis to form stannites and stannates and tin, therefore, belongs to the class of salts just mentioned, and it very soon became evident that these salts do actually possess the power of combining with the fibre to a greater extent than any of the salts which had previously been experimented with.

In one experiment it was noted that a piece of flannelette, which had first been saturated with a solution of sodium stannate and dried, and afterwards similarly treated with a solution of zinc chloride, was quite non-inflammable. After the sample had been subjected to a vigorous washing with soap and water a considerable amount of the fireproofing still remained because, when a light was applied to the cloth, it only ignited with difficulty, burned very slowly, and either went out of itself or was easily extinguished on shaking the material.

This development was so promising that the experiment was repeated in a great variety of ways but, although several results were obtained which were much better than anything which had been seen before, it was disappointing to find that in all the cases the greater part of the fireproofing was lost after repeated washings.

In a later series of experiments the first solution was again sodium stannate and the second consisted of sodium tungstate, zinc acetate and sufficient acetic acid to prevent precipitation of the zinc tungstate formed. The result in this case was so good, the material being practically as safe as wool, even after repeated washings, that the first commercial permanently fireproofed flannelette which was placed on the market was made on these lines.

It was soon found, however, that the material thus treated had two serious drawbacks: it had a tendency to go damp, and an unpleasant smell of acetic acid remained even though the material had been steamed and washed, after the fireproofing process, before being sent out. And apart from these two faults, the fireproofing was still not sufficiently permanent and the cost of the process was too great for it to be considered a satisfactory one.

A further series of careful comparative tests seemed to indicate that the undoubted advance which had been made was mainly due to the use of the stannate and it was, therefore, decided to carry out a series of experiments using salts of tin exclusively.

The fabric after being treated with sodium stannate as before, was, in the earlier of these experiments, passed through a fixing bath containing stannous chloride. A very permanent fireproofing was again obtained but the stannous chloride being a reducing agent tended to destroy or affect the colors of the material and the process would, therefore, be generally applicable only to white cloth.

In order to get over this difficulty, stannic chloride was employed, instead of the stannous salt, as the fixing agent, and to avoid any tendering of the material care was taken that the stannic chloride solution should be of such a strength that a little stannate was left unchanged in the material.

An excellent fireproofing was again obtained, for not only did the material show very little tendency to inflame after it had been washed several times with soap and water, but it had also in such other respects as appearance and feel almost ideal properties, the only objectionable feature being a slight tendency to dust on rubbing and shaking. Now in this particular experiment, in which sodium stannate and stannic chloride had been em-

ployed together, the substance which must have been produced in the fibre, and to which the fireproofing must, therefore, have been due, is stannic oxide and it seemed clear that this oxide or its hydrate must have some remarkable power of combining with, or attaching itself to, the fibre, which enables it to resist removal by washing and rubbing.

But this process still left something to be desired on the score of economy. A certain amount of the tin was undoubtedly wasted, for, in addition to that lost through a portion of the stannate being left unfixed, it was noticed that a considerable amount of the tin oxide, which was formed by the action of the alkali of the stannate on the stannic chloride, was not permanently fixed in the fibres of the material, and was, therefore, removed during the subsequent washing. Tin is so expensive that, in a process to be commercially successful, this loss must obviously be avoided.

There are many ways in which stannic oxide may be precipitated from sodium stannate and one of these, commonly used in ordinary analytical chemistry, consists in adding certain soluble salts such as sodium sulfate or ammonium nitrate to the solution of the stannate, when the whole of the tin is precipitated as oxide or hydrate. In order to find out whether some process of this kind would precipitate this oxide in such a condition that it would remain permanently fixed in the fibre, a number of pieces of flannelette were soaked in sodium stannate and, after thoroughly drying, separately passed through various solutions containing sodium or ammonium salts at the ordinary temperature and at temperatures up to the boiling point. Although, as was to be expected, the results were not uniformly good, a certain degree of permanent fireproofing was always achieved and consequently the matter was systematically followed up with the result that a process was gradually evolved which yielded material possessing quite remarkable properties. The process is briefly this:

The flannelette (or other material) is run through a solution of sodium stannate of approximately 45° Tw. in such a manner that it becomes thoroughly impregnated. It is then squeezed to remove the excess of the solution, passed over heated copper drums in order to thoroughly dry it, after which it is run through a solution of ammonium sulfate of about 15° Tw. and again squeezed and dried.

Apart from the precipitated stannic oxide, the material now contains sodium sulfate and this is removed by passage through water; the material is then dried and subjected to the ordinary processes of finishing. A long series of trials, carried out under the most stringent conditions, have conclusively proved that material subjected to this process is permanently fireproofed. No amount of washing with hot soap and water will remove the fireproofing agent, or in other words, the property of resisting flame lasts as long as the material itself lasts. I will demonstrate this by exhibiting four different specimens: (1) material as it leaves the process and before washing; (2) material which has been washed ten times by hand; (3) material washed 20 times in a machine in a laundry; and (4) a portion of a garment which has been in actual use for 2 years, washed every week and is, as you see, in rags. This extraordinary property of resisting soap and water seems to me to indicate that the oxide of tin is not present merely as an insoluble precipitate in the cloth but must have entered into some actual combination with the fibre, yielding a compound which is not broken down by the action of the weak alkali of the soap. But a matter of hardly less importance, from the practical point of view, is that the material is not only permanently fireproofed by the process I have just described, it also retains and acquires properties which make it as perfect a material in all other respects as could be desired. In the first place the treatment has no effect on the delicate colors which are now so generally employed in connection with the manufacture of flannelette and other cotton

goods, and very careful experiments have demonstrated the fact that the insoluble tin compound in the fibre has not the slightest deleterious action on the most delicate skin. In addition, the presence of the tin compound in the pores gives the cloth a softer and fuller feel than that of the original flannelette and what perhaps is the most unexpected result is the fact that the material is considerably strengthened by the process.

A series of tests made by the Manchester Chamber of Commerce proved that the tensile strength of flannelette is increased nearly 20 per cent. as the result of the introduction of the tin compound into the fibre.

Further and very exhaustive tests made at the Municipal School of Technology, Manchester, on a machine specially designed for testing the wearing properties of fabrics, showed an even greater gain in durability in the case of the fireproofed flannelette. These separate and independent tests conclusively showed that the increase in strength and durability was approximately equal to the cost of the fireproofing treatment so that garments made from the permanently fireproofed flannelette are as a matter of fact no dearer than those made from ordinary flannelette and are, at the same time, as safe as if made from flannel. Some of these properties and statements may be easily tested by each of you independently with the samples in the little book which you received on entering the Hall.

This permanently fireproofed flannelette is now manufactured on the large scale by Messrs. Whipp Bros. and Tod in Manchester under the name of "Non-Flam" and, although its introduction has been slow, it is being increasingly used and will, in all probability, ultimately entirely replace the ordinary inflammable variety. One of the difficulties experienced in connection with its general introduction is the fact, that, owing to the high price of tin, which is now quoted at about £210 or \$1050 per ton, the cost of the process is not inconsiderable but, even with tin at this high price, the extra cost is not more than two cents per yard or about three or four cents for a child's garment. I have here on the table rolls of "Non-Flam" of different qualities so that any one who wishes for a larger sample than is contained in the little book can easily obtain it.

It is hardly necessary for me to say that this process can be applied to any cotton fabric and is especially valuable in connection with muslin because this material is so often used, especially on the stage, for dresses which, on account of their flimsy nature, are naturally highly inflammable. I have here two strips of the same muslin, one of which has been treated by the "Non-Flam" process without in any way affecting its ordinary properties and was then washed 10 times and the difference in inflammability of the two samples is very striking. While the first sample is highly dangerous, it is difficult to imagine that harm could come to any one who happened to be dressed in the treated material even if, by accident, a lighted match came in contact with the dress. Another direction in which the process may be used with great advantage is in connection with lace curtains. Many disastrous fires have occurred by reason of the ignition of lace curtains and there can be no doubt that the greater majority of these would have been avoided if the curtains had been treated by the "Non-Flam" process. As an example of this, I have here a strip of lace curtain which has been subjected to the process and then washed a number of times, and it will be seen that if such material did accidentally come in contact with a lighted match, the danger of fire is reduced to a minimum because even supposing the material did catch fire, the flame is put out at once by the least shake.

It seems to me that it is obvious that, if this process or some other process capable of giving the same protection from fire, were adopted in the case of all inflammable cotton goods and especially in the case of material used for garments, many disastrous fires and the appalling loss of life, especially among young children, might be avoided, and it is for this reason that I have

ventured to bring the subject of the permanent fireproofing of cotton goods to your notice this afternoon.

COAL TAR LIGHT OIL IN THE UNITED STATES: THE MANUFACTURE, NATURE AND USES OF PRODUCTS DERIVED THEREFROM¹

By JOHN MORRIS WEISS

Introductory.—This paper is an attempt to give a rather general outline of that part of coal tar refining dealing with the lighter oils obtained in the first distillation of coal tar. The writer has taken as his theme the so-called "coal tar light oil," and has, in the general description, written as if this were the only source of the refined products mentioned. It must not be forgotten that other products are used as raw materials for the same purposes, and are mixed with light oil products at various stages of manufacture. Thus, coal tar carbofic oil, water gas tar light oil, crude benzol from washing coke oven gases, and Pintsch gas drips may serve as raw materials to be introduced at some point or other in the manufacturing processes.

The figures given for production include products from all these sources, and are not confined to light oil products alone. The figures are the result of compiling as much information as the writer was able to obtain from various manufacturers.

Light Oil Production.—Light oil is produced in the first distillation of coal tar, being the first fraction of oil taken off. In practice, it usually consists of that portion of oil collected while the water is being removed. The amount of light oil obtained from different tars varies considerably, some containing only a trace, while in others it may run as high as 4 per cent. A fair average for coal tars distilled in the United States is about 2 per cent.

Nature of the Material.—Light oil of coal tar, as produced in the United States, varies in composition, depending on the nature of the tar from which it is produced, and upon the method of distillation used. In all coal tar light oil we meet with the same constituents, but their proportions can vary quite widely.

The main constituents of coal tar light oil can be roughly grouped into four classes:

1. Neutral hydrocarbons of the aromatic series.
2. Unsaturated hydrocarbons of various series, the main one, however, being of the styrolene type.
3. Basic bodies, consisting of pyridine and the higher homologues.
4. Acid bodies known as "tar acids," here consisting of phenol and the three isomeric cresols, with small amounts of their higher homologues.

Besides bodies falling into these classes, there are small amounts of other materials such as carbon bisulfide, various organic nitriles and various sulfur compounds, such as thiophene, etc. All the materials manufactured from light oil in the United States fall in the first and fourth classes mentioned above.

Methods of Testing Light Oil.—The assay of light oil usually consists in:

1. A distillation, which gives the approximate amount of hydrocarbons boiling at various temperatures.
2. Determination of tar acids.
3. Determination of tar bases.
4. Determination of naphthalene.
5. Determination of specific gravity.

These tests, with the exception of that for tar bases, have been described in detail, with drawings of the apparatus used, by Mr. S. R. Church (*THIS JOURNAL*, 3, April, 1911). The tar base test is carried out in exactly the same manner as the test for tar acids, preceding this in the analytical process, with the exception that 20° B. sulfuric acid replaces the 10 per cent. soda used in the corresponding tar acid test.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

In exceptional cases more exhaustive tests are made, which include a very careful fractionation of the light oil neutral hydrocarbons, to determine the approximate percentage of pure benzene and toluene, etc., but as these are but seldom used, it seems well to omit them here.

As a means of showing how widely light oil from various sources can vary, the following tests are given as representing average coal tar light oil produced in the United States:

	Maximum	Minimum	Average
Specific gravity.....	1.002	0.953	0.985
Tar acids.....	18.0%	4.0%	7.5%
Naphthalene.....	29.9%	trace	13.2%
Hydrocarbons boiling below 200° C.....	62.0%	30.0%	48.0%

These tests do not include the determination of tar bases, as this is seldom made. I may say, however, that the bases amount to but one to three per cent. of the light oil.

First Distillation of Light Oil.—This is carried on in iron horizontal cylindrical stills, with a capacity of from 3000 to 5000 gallons, in sizes varying from six to eight feet in diameter, and fourteen to sixteen feet in length. The stills are set in brick work with either oil or coal firing. The type of setting has changed from time to time, the most approved type at present being that with a firebrick arch, the hot gases of combustion passing under the arch to the back and then over it under the still to the stack at the front. The stills are provided at the top with a vapor pipe, an opening for charging and a man-hole for cleaning, at the bottom with a draw-off for removal of the residue. The vapor pipe runs directly to the condenser without any baffling or fractioning device intervening. A thermometer set in the vapor pipe of the still serves to regulate the fractions taken off. The distillate is run directly from the condenser into tanks or pans, depending on its nature.

In this first distillation, the light oil is split into but two fractions, one, crude naphtha, up to about 200° C., taken off into a storage tank, and above that point, naphthalene oil, which is run directly into large, shallow iron pans. The residue in the still is thick, and is run out when cool and mixed with crude tar. The heavier fraction, containing naphthalene, is allowed to cool to air temperature, when the naphthalene settles out. As much oil as possible is drained off by gravity, and the drained naphthalene centrifuged to further remove oil. These separated crystals form crude naphthalene, the working up of which will be described later. The oil drained from the naphthalene is moderate boiling creosote, containing a high percentage of tar acids, almost entirely cresols and the next higher homologues. This oil is used as the basis of "percentage" carboic acids second quality, as described later, or is artificially frozen to further remove naphthalene, and the frozen, well settled oil, containing about 25 per cent. of tar acids, is used for the manufacture of disinfectants and sheep dips, or as a basis for first quality "percentage" carboic acids.

Treatment of Crude Naphtha.—The crude naphtha is first brought into iron cone-bottom agitators of about 12,000 gallons capacity, and the tar acids removed by treatment with dilute caustic soda solution. This solution of tar acids (mainly phenol and cresols) serves as the raw material for the manufacture of the refined grades of carboic acid, as will be described in a later part of this paper. The naphtha freed from tar acids is then treated in lead-lined agitators with sufficient dilute sulfuric acid to remove basic bodies. At present, owing to the fact that the market for pyridine bases is very limited in the United States, no attempt is made to recover these bases, but the pyridine sulfate liquor is thrown away.

The extracted naphtha is then subjected to fractional distillation under vacuum of about 29 inches, using a column. This is carried out in stills of the same size and type as used in the first distillation, a column and reflux condenser being used between the still and the condenser. The fractions are collected of necessity in closed receivers. This distillation is regulated,

like the other, by a thermometer in the vapor pipe. Four fractions are taken off:

1. Crude benzol and toluol fraction.
2. Intermediate fraction to be re-run.
3. Crude solvent naphtha fraction.
4. Heavy naphtha fraction.

The residue left in the still is re-run in the crude straight pipe stills as described in the first distillation of light oil. The crude benzol and toluol fraction is re-run in a vertical still with a steam coil and column, and separated into:

- 1A. Crude benzol.
- 1B. Intermediate fraction to be re-run.
- 1C. Crude toluol.

All is gradually accumulated into fractions 1A, 1C, 3 and 4, which come into commerce as "straw color benzol," "straw color toluol," "crude solvent naphtha," and "heavy naphtha."

Refined Benzols from Crude Fractions.—The crude fraction is placed in an iron cone-bottom agitator provided with a mechanical stirring device of the propeller type, and there treated with sulfuric acid, the amount varying with the nature of the material. The sulfuric acid polymerizes and removes in the form of tar the unsaturated hydrocarbons, leaving the aromatic hydrocarbons practically untouched. After the sulfuric acid treatment, the acid is carefully drawn off, together with any tarry matter which collects immediately above the acid. The acid treatment is followed by a treatment with dilute caustic soda to remove small amounts of acid left on the sides of the agitator and mixed through the oil. It is then run to a vertical still, provided with steam coil and live steam. In the case of the lower boiling materials, crude benzol and toluol, the distillation can be carried on almost entirely without live steam, but with the higher boiling materials live steam is necessary to complete the distillation. The product of this distillation is refined 90 per cent. benzol, from the crude benzol fraction, commercial toluol from the toluol fraction, refined solvent naphtha from the crude solvent naphtha fraction, and 200° naphtha from the heavy naphtha fraction. Fifty per cent. benzol and 100 per cent. benzol are made in a similar way by altering as necessary the distilling points on the crude column distillation of fraction No. 1, as denoted above.

The 50, 90 and 100 per cent. benzols consist mainly of benzene and toluene, with small amounts of xylene, and their names are not indicative of the comparative purity of the materials, but merely of the amount distilling at 100° C.

The lower boiling benzols can have the following composition:

	100% Benzol	90% Benzol	50% Benzol
Benzene.....	94-97%	80-85%	40-50%
Toluene.....	2-6%	10-20%	30-60%
Xylene.....	0-1%	0-5%	0-25%

Pure Hydrocarbons.—The manufacture of these consists in taking a refined fraction, such as obtained from the process described in the preceding paragraphs, and submitting it to column distillation in a steam still with a very high column, and taking off a fraction within very narrow temperature limits. Only benzol (benzene) and toluol (toluene) are separated in the pure condition, that is, with less than 0.5 per cent. of impurities. A substance called "pure xylol" is manufactured, consisting of a mixture of the three isomeric xylenes. No attempt is made in this country to separate the three isomers. Pure benzol has about the following composition:

Benzene.....	99.5-99.8%
Toluene.....	0.05%
Thiophene.....	0-0.10%
Carbon bisulfide.....	0-0.02%
Unsaturated hydrocarbons.....	0
Paraffine hydrocarbons.....	0-0.55%

Testing of Benzols.—For a description of the various tests used on benzols, that is, boiling point, specific gravity, flash,

evaporation test, freezing point, and sulfuric acid test, the author has already published these (*THIS JOURNAL*, 3, 10, (1911)), and therefore it does not seem necessary to go into these in detail here.

Properties of Benzols.—These can best be given in tabular form, and we present here the average distillation tests, specific gravity, flash, evaporation, sulfuric acid tests, etc., of the refined grades of benzol, and the distillation, specific gravity, flash and evaporation tests of the crude benzols:

PRODUCT	BOILING POINT	SP. GR. AT 15.5° C.	FLASH POINT	EVAPORATION TEST
Pure benzol ¹	80–82° C.	0.881–0.884	Below 0° C.	10 min.
100% benzol	100% at 100° C.	0.875–0.884	Below 0° C.	13 1/2
90% benzol	90% at 100° C.	0.875–0.882	Below 0° C.	14
50% benzol	50% at 100° C.	0.871–0.875	Below 0° C.	23
Pure toluol	110–112° C.	0.869–0.871	Below 0° C.	29
Commercial toluol	90% at 120°	0.869–0.872	Below 0° C.	33
Pure xylol	135–145°	0.865–0.867	30° C.	89
Solvent naphtha	90% at 160°	0.864–0.870	25.5°	107
Straw col. benzol	85–90 at 100°	0.862–0.870	Below 0° C.	18
Straw col. toluol	85–90 at 120°	0.862–0.870	Below 0° C.	36
Crude solvent	85–90 at 160°	0.876–0.887	25.5° C.	121
Heavy naphtha	85% at 200° C.	0.925–0.940	43° C.	303

¹ Pure benzol has a solidifying point of 5.15 to 5.40° C.

Sulfuric Acid Tests (Water-white grades only).—Pure benzol and toluol, at most pale straw in acid 100 per cent., 90 per cent., 50 per cent., and commercial toluol, yellow in acid, oil white. Solvent, red in acid, oil pale yellow.

Uses of Benzols.—In general, the use of all grades of benzols can be summed up in one word, "solvents." They are excellent solvents for gums, resins, greases, rubber, etc., and it is mainly upon the wide and varied solvent power of benzols that the capabilities for their commercial utilization rest. Pure benzol and pure toluol are used as a basis for manufacturing other chemicals, nitrobenzol, aniline, benzoic acid, saccharin, etc., which in their turn are used generally in dye and drug manufacture. Pure benzol and toluol are also used as solvents in cases of continuous extraction where a low-boiling solvent of great uniformity is required. Pure benzol is also used for the manufacture of special rubber cements where a very high grade of purity is necessary.

It seems better to classify the uses of the other grades of benzol by the industry in which they are used, rather than by the grade of the material, as the same industry may use a varied number of products for different purposes.

Rubber.—Benzol is a perfect solvent for crude Para rubber, being equalled in this respect only by carbon bisulfide. The advantages of benzol over this solvent in regard to safety, etc., are so patent they they need no mention. Therefore, in rubber work where a high-grade cement is demanded, benzol is almost universally used. This is particularly the case in the manufacture of automobile tires, and large amounts of benzol are consumed in this industry.

Rubber solutions, too, are used for the manufacture of insulating varnishes, and benzol finds application here, also as a solvent. A use in connection with rubber work which has not been very extensively applied as yet in the United States, is the cold vulcanization of rubber in which the active agent is sulfur monochloride dissolved in benzol. The use of benzol in this instance depends upon the fact that in addition to being a rubber solvent, it is unaffected chemically by the sulfur monochloride. For most of the rubber purposes, the crude benzols have no application. It is mainly the refined grades that are used, with the lower boiling benzols in greatest use.

Paint and Varnish.—The uses of the various grades of benzol in the paint and varnish industry are quite varied, and of late it has been replacing petroleum benzine as a constituent of turpentine substitutes, owing to its greater solvent properties. This is particularly true in certain varnishes where gums, such as Manila, are used, which are not held in solution properly by benzine, but which are perfectly soluble in benzol.

In straight pigment paints, benzol has not found wide application as yet, but it has been found of considerable advantage as a thinner in paints designed for painting resinous woods, owing to the penetration or "tooth" given to the paint. This use has been very well described in a paper by J. Dewar, published in the *Proceedings of the Convention of Master House Painters and Decorators Association of Pennsylvania*, January, 1911, printed in the *Painters' Magazine* for March, 1911.

Enamel paints, as well as bronze and aluminum paints, also afford a use for benzol. These paints usually have a concentrated solution of Damar gum as their base, and benzol is an ideal material for this purpose, owing to its very strong solvent action on this gum.

Wood stains and stain solvents also have benzol in their makeup. This use is based on the fact that benzols are excellent solvents for oil-soluble aniline colors, and that by the use of benzol, very good penetration into the wood can be obtained.

Paint and varnish removers are to a great extent essentially a mixture of benzol with wood alcohol, and many patents cover the use of benzol in this connection. For these preceding purposes, mostly water white or refined grades are used, and the grade selected depends generally on the evaporative effect desired, in view of the fact that the solvent power of the various grades is approximately the same.

In a few cases in the paint and varnish industry, straw color benzols and the darker, heavier naphthas are used. As examples of this, tar paints, gilsonite paints, ship bottom paints, etc., can be mentioned. In all these the base of the paint is dark, and therefore the color of the solvent used is of no consequence.

Lacquers and Imitation Leathers.—The writer has classed these two industries together, owing to the fact that the application of benzol is based on the same property in both cases. Benzol by itself is not a solvent for pyroxylin, or soluble cotton. However, if a concentrated solution of pyroxylin in amyl acetate is prepared, this solution can be thinned to a greater extent by benzol than any other commercial solvent, without causing the pyroxylin to be precipitated as a gelatinous, insoluble mass. Numbers of lacquers consist merely of such a concentrated solution of soluble cotton thinned to the utmost degree with benzol. In the imitation leathers in many cases, such a solution is applied to cloth, allowed to dry, and then colored and grained. Besides the pyroxylin imitation leathers, there are also others which have a linseed oil base, and in these also benzol is used for solvent purposes.

Miscellaneous Uses.—It hardly seems worth while to the writer to go into any great detail as to the various other uses of benzol much more than a brief mention. Extraction of greases from very varied materials, such as wool, garbage, etc.; extraction of vegetable oils from seeds or press waste; as a constituent of metal polishes, of special metal protective coatings, dry cleaning and scouring; extraction of alkaloids and crude drugs; waterproofing compositions for cloth, etc. As yet it has not been used as a fuel or for motor purposes in the United States, this phase being yet in an experimental stage. In all these uses, the grade of benzol varies according to the particular needs of the process in which it is used.

Production and Distribution of the Use of Benzols, 1910–1911.—In 1910, the production of coal tar solvents of all grades amounted to about 1,500,000 gallons, and in 1911 this was increased to very nearly 2,000,000 gallons. All of this, as noted before, was not produced from coal tar light oil. This was distributed among various industries approximately as follows:

Paint and varnish.....	47.0%
Rubber and rubber cements.....	18.0%
Imitation leathers.....	10.0%
Chemical manufactures.....	11.0%
Miscellaneous and undetermined.....	14.0%
	100.0%

Of course, these figures are only approximate, but are indicative of the magnitude of the coal tar solvent industry in this country.

Working up Carbonate to Crude Carbolic Acid.—The soda solution of tar acids obtained in the working up of light oil serves as raw material for the manufacture of various refined carbolic acids. The carbolate is first boiled to remove mechanically dissolved hydrocarbons. This is, in some cases, performed in an open tank, with coil and live steam; in more improved forms of apparatus, vacuum pans are used for this purpose. From the carbonate thus purified, carbolic acid is liberated with carbon dioxide gas obtained from a furnace burning a mixture of coke and limestone. When the carbolate is sufficiently blown, a clear separation takes place, the upper layer being crude carbolic acid, and the lower, carbonate of soda. The carbonate of soda is treated in another agitator with lime obtained from the carbon dioxide furnace, filter-pressed, and the regained caustic soda used over again in future operations. The crude carbolic acid thus obtained contains from 12 to 16 per cent. water, and from 4 to 5 per cent. of non-volatile residue, the main amount being phenol and cresols.

Refined Carbolic and Cresylic Acids.—The crude carbolic acid is distilled in a vacuum column still, taking off first, water, then a fraction rich in phenol, an intermediate fraction to be re-run, and a cresylic fraction. The cresylic fraction is redistilled in a still using a block-tin condenser and receiver, and comes on the market as "white cresylic acid," or, if fractionated to a close boiling point, as U. S. P. cresol.

The first fraction, rich in phenol, is cooled to a suitable temperature, and the phenol crystallizes out, and after draining and centrifuging, requires only a distillation, using, as in the case of white cresylic, a block-tin condenser and receiver, to be marketed as "crystallized carbolic acid," with a melting point of 39° to 40° C. The liquid drainings from the crystal acid are re-run in the column still similarly to the crude acid.

Other Commercial Carbolic Acids.—Various other grades of carbolic acid are known as "95 per cent. dark," "97-99 per cent. straw color," and various so-called "percentage" acids, 15, 25 and 50 per cent., etc., first and second quality. These are obtained from the drained oil from crude naphthalene. The 95 per cent. dark is a dark-colored carbolic acid, containing at least 95 per cent. of bodies soluble in soda, the remainder being made up of water and neutral hydrocarbons.

The 97-99 per cent. straw color acid consists merely of the 95 per cent. dark distilled under vacuum to remove water and slight amounts of tarry matter, and contains as its only impurity neutral hydrocarbons.

The percentage acids are creosote oil with various guaranteed percentages of tar acids, and are obtained by simple mixture.

The second quality acids deposit naphthalene if chilled, whereas the first quality are free from naphthalene down to at least 32° F.

Methods of Testing Carbolic Acids.—The percentage acids are usually tested only for water, percentage of tar acids, and deposit of naphthalene at 32° F. The tar acid test consists in distilling 100 cubic centimeters of material from a bulb and noting the shrinkage of the distillate when treated with 10 per cent. caustic soda. Water is determined in the distillation. A small sample is also cooled in a tube to 32° F. for some time to note if naphthalene separates.

Ninety-seven to 99 per cent. straw color acid and 95 per cent. dark are merely tested for water, specific gravity, distillation (similar to benzol distillation) and matter insoluble in soda.

Crystall carbolic acid is usually tested by the methods as given in the United States Pharmacopoeia, the length to which these tests are carried varying with the purpose for which the acid is to be used.

Uses of Pure Carbolic Acid and Pure Cresol.—Pure carbolic acid and pure cresol are used mainly medicinally, and in the

manufacture of medicinal preparations. Some carbolic acid is used for the manufacture of picric acid and dyes, and a small amount for leather finishing.

The crude grades of carbolic acids are used in the manufacture of sheep dips and disinfectants, and also in some cases, directly for disinfectant purposes. A small proportion is used in rubber reclaiming and in certain paint and varnish removers. Another interesting use which may be of considerable future importance is in the manufacture of various resinous products by condensation with aldehydes.

Production of Carbolic Acid.—It was impossible to obtain reasonably accurate figures for production and importation of refined and crude carbolic acids. The importations are not well enough classified to obtain the definite information desired, nor was the writer able to obtain full information as to that manufactured in this country, especially in the case of the cruder grades.

Naphthalene Manufacture.—The crude naphthalene obtained by centrifuging the second fraction in the first distillation of light oil is melted up and run out into shallow pans and allowed to cool and crystallize slowly. This recrystallized naphthalene is submitted to a second centrifuging, and is then known as purified naphthalene. A very little goes into the trade as such. For further purification, this naphthalene is distilled and water and tarry matter removed. The middle fraction is run into a lead-lined washbox, and there treated hot with concentrated sulfuric acid, then with water, and finally with soda to remove the last traces of acid. The washed naphthalene is then run back into a still and redistilled, and the middle portion taken as refined naphthalene. The "heads and tails" running from the still are returned to crude naphthalene.

The refined naphthalene is then made into various forms used commercially.

Flake Naphthalene.—This is produced by subliming the refined naphthalene from shallow pans into a large wooden room. The naphthalene is held in the pans at about 160° C. by means of steam coils, and gradually sublimates into the room and condenses on the walls, ceiling and floor. After a sufficient period of time has elapsed, the room is opened, the flake naphthalene removed, and a new operation started.

Naphthalene Balls.—These are made by molding refined naphthalene in suitable molds.

Other Forms.—The flake and balls are the most used forms, but small amounts are put out in the form of crushed crystals, powdered, and various shaped blocks (square, lozenge, domino shape, etc.).

Method of Testing Naphthalene.—Refined naphthalene is tested usually only for melting point. Occasionally a test for coloration with sulfuric acid is made for the very highest grade used for chemical purposes. The most essential features for ordinary purposes is the color, and, moreover, the capability of keeping the white color even in the presence of sunlight. The crude naphthalene are usually assayed by distillation for water and non-volatile residue, in addition to melting point test.

Uses of Naphthalene.—The main use of naphthalene is as an insect deterrent. The well known use of so-called "moth balls," and flake naphthalene requires no comment. A small amount of naphthalene is used in the manufacture of other chemicals, such as naphthol, phthalic acid, etc. However, these latter industries have not as yet been developed to any great extent in the United States.

Production of Naphthalene, 1910-11.—In 1910 and 1911, between six and seven million pounds per year were used in the United States, of which approximately 45 per cent. was produced in this country. At least 95 per cent. is used by the drug trade for sale as a moth deterrent. The remainder is absorbed by manufacturers for divers purposes.

CONCLUSION

The above paragraphs give a general view of the present status of refining light oil in the United States. Besides, at present, some light oil is produced so far from refineries as to make it impractical to transport it to a point where it can be utilized. Such light oil is mostly used up as a thinner in cheap tar paints.

Up to the present, the manufacture of products in this field has been mainly confined to materials already existent in the crude oil, and capable of being isolated by physical and simple chemical means. The further, more intricately chemical manufacture of the various derivatives of benzene, toluene, naphthalene, etc., which serve as raw materials for dye manufacture, has as yet been carried on only in a comparatively small way in the United States.

The chemical possibilities along these lines are yet to be developed in this country, and here indeed is a wide field for technical endeavor which will place the coal tar industry of the United States in a stage of development equal to that already attained abroad.

NEW YORK CITY

THE PAST, PRESENT, AND FUTURE OF THE NAVAL STORES INDUSTRY¹

By CHARLES H. HERTY

The limited use of the oleoresinous exudate of pine trees dates back many centuries, but the real beginning of an industry on a large scale is closely associated with the discovery of the vast pine forests which extend along the southeastern and southern coasts of the United States from North Carolina to Texas.

These forests lie chiefly in the coastal plain and in the slightly hilly country between the piedmont plateau and the coastal plain, a strip varying in width from one hundred to two hundred miles and characterized by a sandy soil, covered for the most part with "wire grass," this furnishing a beautiful carpet of green in spring and summer, but making a serious fire risk in winter. The longleaf pine readily sheds its lower limbs, especially in close stands, so that the forests are remarkably open and free from that undergrowth, which, in the northwest, leads to such destructive forest fires.

The early settlers in eastern North Carolina began the exploitation of their forests of longleaf pine for the purpose of providing tar and pitch for use in the construction of wooden ships, and gradually extended their operations to the collection of crude turpentine which was shipped to northern cities or England for distillation. The forests covered the entire territory and, as clearings for farms were needed, destructive methods of operation were welcomed and encouraged.

At the same time limited operations were being conducted upon the maritime pine in southwestern France between Bordeaux and Bayonne. To receive the crude turpentine the French made use of a hole dug in the sand at the base of the tree. The oleoresin flowing from the wound on the trunk above was collected in these holes. Necessarily by this method much of the material was wasted and rendered impure.

AMERICAN METHOD OF COLLECTION

In North Carolina the method of collection was improved, or thought to be improved, by cutting a large opening, the "box," in the base of the tree. Into this box the crude turpentine flowed and was collected at regular intervals. The conservative character of the men engaged in this industry led to the continuance of this wasteful and destructive method of "boxing" until the very recent past.

Briefly, the method of operating so long in use in the United

States is as follows: In the winter the laborers are engaged in cutting "boxes." Each box is then "cornered," a wide chip being removed from each half of the box to provide a surface suitable for directing the flow of crude turpentine to the box. Meanwhile, other laborers are employed in clearing all combustible material from around each tree, "raking." Ground fires are then started to consume the dead wire grass, chips, etc. With the opening of Spring, "chipping" begins. This consists in scarifying each week the trunk of the tree above the "cornered" surface by means of a "hack," a U-shaped steel tool set in a wooden handle. Attached to this handle is a heavy iron weight to give momentum to the free arm swing used in chipping. After four or five weeks the "boxes" average a good filling and the crude turpentine, "dip," is then transferred to buckets by flat iron paddles, and from the buckets it is collected in barrels conveniently placed in the woods. In the Fall, at the end of the chipping season, the hardened oleoresin, which has gradually collected during the chipping season on the scarified surface of the tree, is removed by scraping, giving thus the name "scrape" to this product, which is sold as "Gum Thus," or distilled. In the following Winter the trees are again raked and the grass fired, and in the Spring chipping is resumed at the point on the trunk of each tree where it ceased the previous year. This cycle is usually continued from three to four years, although in early days it was often continued ten or twelve years, the scarified surface extending high on the trunks. Necessarily the yield from such high chipping was largely decreased, owing to the increased distance of flow to the receptacle.

In the early days of the North Carolina industry, no effort was made to distill the product, but gradually it became clear that it would be better to separate the crude turpentine into spirits of turpentine and rosin by distillation in the woods. For this purpose iron stills were used at first, but results were unsatisfactory until the introduction of copper stills, which were less liable to crack and could be heated with greater uniformity and better control.

The industry now began to grow rapidly and before many years it was found that the supply of available timber in North Carolina was rapidly decreasing. This led many of the operators to transfer their operations to the virgin forests of the adjoining state, South Carolina, where the same destructive methods were applied by the same men or their descendants. In this way, and for these reasons, the center of the industry has gradually moved southward and then westward as evidenced by the relative prominence of the ports for exports of the products: first Wilmington, N. C., then Charleston, S. C., then Savannah, Ga., and now the latter, together with Jacksonville, Fla., and the gulf ports, Tampa, Fla., Pensacola, Fla., Mobile, Ala., Gulfport, Miss., New Orleans, La., and others.

FRENCH IMPROVEMENTS

The steady growth of the American industry received a serious check during the Civil War. The consequent scarcity of the products was accompanied by an abnormal increase in their value. This enhanced valuation led Hugues, a Frenchman, to propose a less wasteful method for the French forests than the hole dug in the sand. He proposed as a substitute a clay pot holding about one pint. This pot was supported on its bottom by a large nail driven into the tree and on one side of its upper rim by a strip of sheet zinc, approximately 2 inches \times 4 inches, slightly curved and driven into a corresponding upwardly inclined cut in the wood. This spout served to direct the oleoresin into the pot. At first his proposition was scoffed at and the peasants amused themselves by breaking the little pots. It is a pitiful commentary that Hugues died in poverty, but his ideas lived and gradually became adopted in France.

AMERICAN IMPROVEMENTS

As the knowledge of the new method in France spread to this

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

country, numerous efforts were made to apply similar forms of apparatus to the American system of chipping, but for many years such efforts failed. No less than fifteen patents were issued in the United States on this subject, but no one of them proved a commercial success.

Eleven years ago the writer began a series of field experiments on a small scale in the turpentine forests of South Georgia. One feature of these experiments was the use of a modification of the Hugues system, consisting of two separate metallic gutters, inserted in upwardly inclined cuts in the tree, along which the oleoresin flows. The upper and shorter gutter is separated at its lower end about one inch from the lower gutter and empties into it. The lower gutter extends from two to three inches beyond the center of the angular scarified surface formed in chipping and serves as a spout to convey the oleoresin to a cup suspended from a nail just below the end of the gutter. These cups are made of either well burned clay or galvanized iron, and have a capacity of one quart.

Attracted by the promising character of these preliminary experiments, the U. S. Bureau of Forestry began a series of field tests of the apparatus on a large scale, the work being under the immediate supervision of the writer. Before the end of the first season of testing it was evident that the apparatus was a practical success, and the results attained, both as to quantity and quality of oleoresin, justified the hope of immediate commercial introduction of the system. But the habits of long years made difficult the adoption of such an innovation. This ultra-conservatism was slowly overcome and the adoption of the new system spread rapidly. Only a few years more will be required to witness the complete replacement of the "box" by the "cup" system in American forests. A detailed account of these experiments is given in Bulletin 40 and Circular 34 of the U. S. Bureau of Forestry.

With the main points at issue settled, namely, improved yields both in quantity and quality of the products and preservation of the trees, other forms of apparatus were devised to meet the objections of some of the operators to certain points in the cup and gutter system. Many of these have never proved practical, but some have been introduced on a considerable commercial scale.

The successful outcome of the experiments on the relative yields from the "box" and the "cup" system led the United States Forest Service to further experiments in more conservative treatment of the trees in chipping. Comparative studies were made of the yield from deep and shallow chipping and the latter found to give the greater yield during a period of four years of operation. Other experiments showed that a less rapid rate of ascent of the trunk also gave larger yields, and experiments combining these several modifications of present practices showed a largely increased yield. A final set of experiments pointed clearly the rational way to a perpetuation of the naval stores industry in America. The details of this investigation are given in Bulletin 90 of the United States Forest Service.

DISTILLATION

In the matter of distillation, only slight advances have been made in America. The uniform process consists in the use of a large copper kettle and condensing worm. The charge for a distillation averages nine to ten barrels of crude turpentine. The kettle is heated by free flame and during the distillation a small stream of hot water from the top of the condenser tub is admitted through an opening in the upper part of the kettle, thus facilitating the removal of the volatile oil. The condensed spirits of turpentine and water separate in the receiver, owing to difference in specific gravity, and the lighter spirits of turpentine is transferred to oak barrels, well coated with glue on the inside. No effort is made to redistill this product, and it always comes upon the market contaminated by a small

amount of resin carried over mechanically during distillation. After most of the volatile oil has passed off, the still cap is removed, excess water in the kettle boiled off, and the molten rosin drawn off through a tap in the bottom of the kettle onto a coarse wire filter, then through a second filter of fine mesh wire overlaid with cotton batting. The molten rosin is then dipped into wooden barrels luted with clay and solidifies on cooling. In this condition it is shipped to market.

The usual method of controlling the distillation is by the sound heard at the mouth of the condenser worm. Within the past three years a number of American operators have substituted for this method that of thermometer control with very excellent results.

In France, much more progress has been made in the art of distillation. Among the French distilleries there are three distinct types: first—a system closely resembling the American; second—distillation solely by steam in steam jacketed vessels; and third—a mixed system in which there is direct contact of fire with the kettle during the first stage of the distillation, then replacement of this by mixed injection of steam and hot water. By this means, a constant temperature is maintained, enabling the complete removal of all spirits of turpentine without danger of scorching the rosin.

It can readily be understood that in France, under proper methods of forestry, with conservative tapping of the trees and provision for systematic reforestation, a distillery can look forward to a permanent supply of raw material. Hence there is justification for the more costly plants and more efficient methods of distillation; but in America, where under past methods the industry shifts so rapidly, so great an outlay of capital for this purpose would not be justified. There is no doubt that with an excellent "stiller" very good results can be obtained under the American system, but the personal element of the stiller enters into the question, and this could be easily avoided without any great outlay of capital by adopting the French system of mixed injection.

Quite recently M. Castets has erected near Dax, France, a distillery which combines the features of continuous distillation in a partial vacuum and condensation by pressure of the waste spirits of turpentine vapors from the ordinary condenser in a second condenser attached to the first, thus increasing notably the yield of volatile oil and improving the quality of the rosin.

THE INDUSTRY IN OTHER COUNTRIES

There is no need of any especial consideration of the Spanish industry, which has developed considerably during the past decade. The operations are essentially the same as the French, and the same species of pine, *Pinus Maritima*, is exploited.

In Austria the industry is more limited and is even more destructive than by the old American system, a "box" being cut in the base of the tree, *Pinus Laricio*, and the trunk of the tree scarified for at least fifty per cent. of its circumference, the oleoresin being directed towards the center of the scarified surface by thin wooden strips inserted in downward cuts in the tree.

In Russia the chief tree exploited is *Pinus Sylvestris*. Climatic conditions do not admit of the usual process of collecting the crude turpentine at regular intervals. Instead, the trees are scarified in Spring over a space about three feet high and almost encircling the tree. During the year a mass of hardened rosin collects on this surface. In the Winter it is scraped from the tree and distilled for its volatile oil and resin. This process is repeated for five years. The tree is then felled and the resinous portion of the tree subjected to destructive distillation. In other districts no effort is made to collect the rosin from the trees annually, but this is allowed to remain until the end of the fifth year of scarification. The tree is then felled and that part containing the rosin distilled first at a low temperature to obtain the volatile oil, then at a more elevated temperature to obtain tar and charcoal by destructive distillation of the wood.

The spirits of turpentine from Germany, Sweden, and Finland seems to be a product solely of the destructive distillation of resinous wood.

The production of naval stores in India and other tropical countries is at present on too small a commercial scale to call for any detailed discussion here.

WOOD SPIRITS OF TURPENTINE

Among the various departments of the naval stores industry in America none has had a more varied and interesting career than that of the production of "wood spirits of turpentine" by destructive distillation of resinous wood. Years ago considerable capital was invested in plants for utilizing the by-products formed during the destructive distillation of "fat lightwood." None of the plants were commercially successful and for a while nothing was heard of the industry. But with the increase in price of spirits of turpentine resulting from the formation of the Turpentine Operators Association in 1902, a fresh impetus was given to the "wood spirits of turpentine" industry. At first somewhat crude methods of destructive distillation were advocated, and as the promoters of this industry appealed largely to local interest in having stumps for distillation removed from fields suitable for cultivation, a double impetus was received. Much enthusiasm was aroused, and a number of plants constructed. But the industry received a serious blow in the refusal of the varnish makers to use the impure "wood spirits of turpentine" manufactured, by the failure to find a market for many of the heavier oils and the coke, and by the destruction by fire of many of the improperly constructed plants.

The price of spirits of turpentine continued to rise and led to the development of the steam extraction process for manufacture of wood spirits of turpentine. After thorough grinding, the wood is treated in iron retorts with steam, and the volatile oil distilled, no effort being made to obtain any other product. By one redistillation of the product a very high-grade spirits of turpentine is obtained, equal, if not superior, to that from the living tree. Unfortunately, the yield is not sufficiently large to make the process remunerative.

Quite a different process is employed by those plants which utilize a bath of molten rosin for removal of the spirits of turpentine from the wood, with subsequent distillation of the volatile oil from this bath. Such plants seem to have met with a fair measure of success.

More recently, extraction processes have been developed which employ low-boiling petroleum products as the extractive. Such plants recover both the spirits of turpentine and the rosin from the ground wood, and have a great advantage in the present very high value of rosin. These plants are also utilizing the refuse from the straining of rosin at the distilleries in the woods, a product formerly burned on the waste piles, but now bringing nineteen dollars per ton. This method is adding a considerable amount to the annual output of rosin.

The most recent development is a plant for destructive distillation of wood in retorts heated by jackets filled with high-boiling petroleum fractions. By this means the fire risk is practically completely eliminated and the results indicate that by means of the complete and ready temperature control of the oil jacket larger yields of better products can be obtained.

ANNUAL PRODUCTION OF NAVAL STORES

No subject connected with the naval stores industry admits of so little accuracy of statement as does that of statistics on the total annual production. The most careful estimates are at best only approximations. This is unfortunate, for in the past it has frequently led to speculative manipulations of the market and the temporary establishment of values which had no legitimate basis depending on supply and demand.

The following table of annual production is given, therefore,

as an approximation only, but it is believed to be a reasonably accurate approximation:

	Spirits of turpentine barrels (52 gallons)	Rosin barrels (500 lbs)
America.....	600,000	2,100,000
France.....	100,000	350,000
Spain.....	25,000	87,500
Austria.....	3,000	10,500
Other countries.....	50,000 (?)	(?)
Total estimated production	778,000	2,548,000

PRODUCTION OF CRUDE TURPENTINE PER TREE

Here again definite figures are difficult to give, for there is no reliable information concerning the number of trees in operation. Furthermore, there is often very wide variation in the producing power of adjacent trees* of the same species, size, and crown. But from the data in the publications of the United States Forest Service, an average American pine, worked under the cup system, will produce, during four years of operation, an annual average of ten pounds of crude turpentine and two and a half pounds of "scrape," the proportionate yield being considerably greater during the first and second than during the third and fourth years of operation.

The average daily flow of crude turpentine during one week from a freshly chipped surface on such pines is shown in the following table, the results having been obtained during the summer of 1901 on trees near Statesboro, Georgia:

Day	Yield per tree (grams)			Average yield (grams)	Per cent. average yield
	1	2	3		
1	113.0	46.5	89.0	82.8	62.9
2	22.5	7.5	16.0	15.3	11.6
3	13.5	6.5	16.0	12.0	9.1
4	9.0	5.0	17.0	7.0	5.3
5 & 6	9.0	5.0	23.0	12.3	9.3
7	1.0	2.0	4.0	2.3	1.8
Total	168.0	72.5	165.0	131.7	100.0

TSCHIRCH'S VIEWS ON RESIN FLOW

As to the seat of resin production and cause of resin flow, most valuable and important views have been advanced by Prof. A. Tschirch in his book, "Die Harze und die Harzbehälter," 2nd edition. Tschirch has shown that the seat of resin production is a mucilaginous layer lining the inner walls of the resin ducts. These ducts he divides into two classes: First—primary ducts, whose resin is to be considered a true physiological product. Such ducts occur irregularly and in varying number in any pine. They play only an insignificant rôle as producers of commercial crude turpentine. Second—secondary resin ducts which form in large numbers in the outer layers of the new wood after a tree is wounded, both above and below the wound. Their oleoresinous exudate is, therefore, a pathological product. It is from such pathological ducts that the great bulk of crude turpentine is obtained.

The application of these views to practical problems in the turpentine forests has already yielded important and fruitful results.

FUTURE OF THE INDUSTRY

During the past few years the statement has frequently been made that from present indications the naval stores industry must cease to exist, at least as a large industry, within the next twenty years. While it is true that there are danger signals which must be heeded, such pessimistic views do not seem to be well grounded.

Certainly in France and consequently in Spain, where the same system is in operation, the industry has been placed upon a self-perpetuating basis.

In America we have been prodigal with our wealth of virgin forest. But it must be remembered that until the last decade these forests have had a very low commercial valuation. The average

price for well timbered lands in our southern states not many years ago was approximately one dollar per acre, land, timber, and all. Indeed, the popular term applied to all holders of large tracts of such lands was "land poor," as expense of taxation, protection, etc., exceeded any hope of probable profit. This condition was largely due to lack of transportation facilities, insecurity of title, low price of naval stores and lumber, lack of knowledge of the farming value of much of the land on which these forests stood, and the belief that the forests were inexhaustible.

Now conditions have entirely changed. Railroads penetrate every portion of the territory, titles have been cleared, prices of naval stores have brought wealth to the operators, the lumbermen from Michigan, Wisconsin, and other northern states have turned from the rapidly disappearing white pine forests of the north to those of the southern yellow pine; where forests once stood farms have been developed which surpass in fertility any other portion of the southern states, and a clear knowledge has been gained that the forests are by no means inexhaustible. Furthermore, the spirit of conservation of natural resources has made itself felt in this field as well as in those of minerals, water-power, etc.

The consequence of these changes has been a very rapid enhancement in the value of such holdings. And with increased valuation comes naturally the desire to protect and use conservatively. Unquestionably, the stand of virgin forest will still further diminish, for the demand for farm lands is active, the call for lumber imperative, and the danger of tropical storms along the Gulf Coast ever present. With such diminution in supply will come still further enhancement in values and still more conservative methods of operation.

So much for the present stand of virgin forest. If the situation was limited to this alone, the outlook might be considered gloomy. But it must be remembered that there are vast tracts of cut-over lands in portions of the southern states whose clay sub-soil lies so deep that the lands are not suited to agriculture. On such lands the longleaf pine, with its long tap root, prospers. Magnificent forests once covered every acre of such lands and fortunately tree planting is not required to reproduce such forests. Nature alone will again cover this territory with a wealth of forest, provided nature is given an opportunity; for the most superficial observer who travels through this territory will testify that where conditions have been favorable natural reproduction has brought again splendid, though small, young forests.

Against this willingness of nature to restore this rich heritage to us, stand three agencies.

First, and of least importance: The consumption by hogs of the delicately flavored and nutritious feed of the longleaf pine. This is a real factor in certain somewhat restricted districts. The constantly spreading sentiment for "stock laws" will check this evil.

Second, and of the very greatest importance: The destructive action of the ground fires, which annually sweep over the entire turpentine belt. Such fires destroy the myriads of young seedlings which can readily be seen springing up in the wire grass which surrounds them on every side. The seedling devotes the greater part of its early energies to sending down its long tap root through the deep sands rather than to strengthening its stalk above ground; hence, in most cases, it is not able to withstand the constantly recurring ground fires. The doctrinaire may rail against the evils of such firing of the woods, but from one who has lived among the turpentine camps there comes no word of reproach against the turpentine operator who "burns the woods." His all is invested on the outer surface of his trees. A serious outbreak of fire during midseason means financial ruin. The carelessness and sometimes viciousness of laborers is too serious a risk to run with a mass of dead wire

grass covering every foot of his territory. Naturally he protects himself by burning this grass when he is prepared for it, after "taking season."

Where then is the hope for reforestation? In the realization of the value of the waste cut over lands where turpentine operations cannot be carried on for lack of timber. Such lands have now but little value, but the lesson of France shows that even there a reasonable income begins from artificial reproduction within a period of twenty years and then rapidly increases. With our warm southern climate the prospect for rich returns from such investments should be even greater than in France.

Third, The greed of man. If we are to have a self-perpetuating industry, even stock laws and the reforestation of waste lands will not avail if a practice on the part of turpentine operators during the past two years continues. The abnormally high price of spirits of turpentine two years ago led to a wild scramble for timber for increased operations. At the same time the efficiency of the "cup" system was just gaining wide recognition. Realizing that a tree too small to have a "box" cut in it could be worked with a cup hung upon it, the operators throughout the whole region proceeded to cup every small tree to which access could be gained. In many cases new farms were opened on old abandoned territory where natural reproduction had furnished thrifty young forests. The result was overproduction of crude turpentine. The temporary benefit to the consumers in the drop in values following this overproduction was dearly bought, for the price was the destruction of young forests which, in time, should have produced their full share of the world's need of spirits of turpentine and rosin. Common sense must and will govern in this matter. It is only necessary for the operators to realize that the yield from such saplings does not meet the cost of production; then the practice will cease.

Surely the above considerations justify an optimistic view of the future of the naval stores industry. But experiment, demonstration, statistics, and knowledge of progress made in other lands, must lead the way for the man in the woods.

UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL

THE TECHNICAL PROBLEMS OF COAL PREPARATION¹.

By W. S. AYRES

The problems involved in the preparation of coal begin in the mine itself and before the coal is even cut, and end with the loading of the prepared product into transportation cars ready for market. For the solution of these problems the engineer must bring to his aid geology, petrology, mineralogy, chemistry, hydrostatics, pneumatics and mechanics. These sciences have, after much study and a long-continued experimentation with every variety of coal, divulged the limits within which their respective groups of natural laws can be used for the accomplishment of the end sought. Any practice outside of these definite limits is sure to lead to disaster.

Having these guiding principles at hand, the continuity, uniformity, and structural nature of the beds of coal are determined, from which the system of mining and cutting is formulated; the physical peculiarities of both the coal and the refuse are carefully studied and the methods of handling and preparation are definitely selected; the degree of purity possible in the preparation, the possible percentage of recovery, the economy of the process adopted, and the market value of the prepared product are also determined.

In the mine it is of great importance to first determine the recoverable tonnage in the coal beds, and from this data to determine the daily capacity of the proposed preparation plant.

The method of mining the several seams should be governed chiefly by the manner in which the refuse is associated with the

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

coal. The breaking of the slates and rock into small pieces, in the cutting or blasting of the coal, must be avoided as much as possible for the reason that the larger the pieces of refuse and the smaller the quantity of it that is finely broken the simpler and less expensive the preparation of the coal for market will be. Wherever a shaly roof clod is free to fall as soon as the coal is removed, every economic means should be resorted to to prevent it from mixing with the coal.

But it is also of very great importance in the preparation problem to determine what alterations, if any, have taken place in the coal beds from folds in the strata. These folds, wherever found, have altered to a greater or less degree the fracture of the coal. In many cases they have crushed the coal almost to a powder, particularly where they occur in the anthracite and semi-anthracite fields. In others, the folding has caused a shale-like fracture of both the coal and slate. Upon the presence of the flat fractured material, in considerable quantity, chiefly depends the selection of the preparation scheme. There are some other conditions, however, which may materially modify that selection, namely, the manner in which the refuse is associated or combined with the coal. It may be associated in a very simple way, consisting of bands of slate or rock a half inch or more in thickness, which separate from the coal, in the process of mining, by distinct dividing planes, or it may be combined with the coal without any partings, and can be separated from it only by hand tools or by repeated crushing in the preparation plant.

As to the transportation of the material from the working places in the mine to the preparation plant, it should be done in closed-end cars. The method of handling closed-end cars at the dump is simple enough after full provision has been made for the system. The saving of coal filtered through the doors along the gangways and haulage tracks, the saving in labor necessary to periodically clean up these tracks, the avoidance of accidents from the doors springing open, the saving in repairs to the mine-cars because of the absence of the car doors, and the safer condition against dust explosions would pay a dividend over any advantages that may exist in favor of the open-end or door-car.

The preparation of coal, whether anthracite, bituminous or lignite, or any of the grades between or beyond them, must make use of the same natural laws, namely, those governing the difference in specific gravity and those governing the difference in the angle of repose. One of these groups may be perfectly efficient in preparing one coal having certain physical characteristics, while for another coal the other group would do perfect work, and for the almost infinite mergings of the two typical classes of coal a series of combinations and modifications of the two principal methods would have to be employed.

In the anthracite fields of Pennsylvania, the preparation of coal has been carried to the highest degree of efficiency and economy known to the world, yet the problem in all its details is not yet satisfactorily solved.

In the earliest days of anthracite mining in Pennsylvania only pure lumps of coal were shipped, and to obtain these only the purest beds of the series or the purest benches of a single bed were mined. The fine coal which would pass through a mesh of about two inches was sent out to the waste-bank. No attempt was made to mine the entire bed, or to systematically prepare the coal either by sizing or by removing the impurities.

The governing factors in the preparation of any coal are, to send the coal to the consumer in a condition suited to his requirements, and at a cost that leaves a margin of profit to the operator. The consumer's requirements are presumably based on the economic results that he desires to obtain, whether they pertain to steam generation, gas production, or metallurgical processes. Therefore, to meet his requirements—which set the standards for sizes and purity—the producer must

search out ways and means, within economic limits, to prepare his coal. The economic end of this problem is not an easy one, and consequently because of the extended and intricate nature of the preparation requirements for some complicated deposits of coal, added to a difficult mining proposition, there is but little profit left to the operator; therefore, it is easy to understand why one operation will not pay a profit, while another with a different deposit pays handsomely. Each must prepare its coal according to the same standards for size and purity, no matter what it may cost, and receive for its prepared product the same market value.

In the specific gravity process of preparation, typified in the jig, many perplexing problems have arisen and many annoying results are always present, depending for their degree of seriousness upon the physical nature of the material being treated.

Any material in order to be treated in the most efficient manner by any process must first be sized. The most efficient method of sizing coal as it comes from the mine—and that sizing must have a very limited range in variation—is by a series of shaking screens. The revolving screen is a thing of the past, because of its inefficiency, its destructiveness to the coal by chipping, and its reversal of the natural order of sizing. The mesh of these shaking screens is circular, and it is self-evident that this circular mesh will allow, but in a less degree than the old square mesh, all conceivable shapes of material to drop through it, provided that each individual piece has for the maximum dimension of its minimum cross-section a measurement just a little less than the diameter of the mesh. The result is that the material as sized contains cubes, pieces that are triangular, round, oblong, rectangular, and square, having thicknesses that are very small compared with their other dimensions, and an infinite gradation of sectional areas between each of these typical shapes and that of the cube. The specific gravity of the slate and rock ranges from 1.90 to 2.50, while the specific gravity of the coal averages about 1.50. It is a very easy matter for any one to demonstrate by a few simple calculations, using the specific gravities of the coal and refuse just given and applying them to the various shapes of pieces given, that a cube of pure coal will tend to pass out of the jig with the refuse, while the thin flat pieces of slate of the lighter specific gravity are sure to float over with the coal. The reason for this is that the ratio of the area of surface of the cube of coal, exposed to the impulses of the water in the jig, to its weight, is greater than the ratio between the area of surface exposed of a thin, light piece of slate and its weight. These very inefficiencies are experienced wherever this class of variformed material is treated by the jig. The inherent conditions make the failure of the jig a natural consequence, and confirm the conclusion from tests that no jig can be made to separate efficiently a material containing a variety of forms, particularly cubical pieces of coal and flat pieces of light slate. Much time and money have been spent in a fruitless endeavor to meet the condition by introducing some new and untried form of jig, with the same inefficient results. A thorough grasp of the technical features of this problem would at once show clearly the limits of the possibilities of coal preparation by this process alone.

The attrition in the jig caused by its rapid pulsations amounts to a serious waste of coal, ranging from 2 per cent. for the very hardest coal to $21\frac{1}{2}$ per cent. for the softest anthracite, or at the present market value of prepared sizes to from 8 to 89 cents per ton. The average loss sustained is estimated to be between three and five per cent. The total loss per year by chippings alone on coal treated by the jig and separating machines causing impact in the anthracite field of Pennsylvania is estimated to be more than three million dollars.

Of the other mechanical devices for removing impurities from coal there are three that are extensively used, each employing

the difference in the angle of repose between slate and coal as the basic principle of its operation.

The first is so constructed that a broad stream of material, about five feet wide and spread out in such manner that the pieces in their forward movement will not touch each other, is intermittently fed upon a short, adjustable incline floor, at the lower edge of which is a narrow section of slate or other gritty material. Immediately below the section of slate is a narrow opening of several inches and beyond this is a continuation of the inclined floor. The action is that the refuse passing over the slate section of the floor is retarded and drops through the narrow opening, while the coal because of its less angle of repose continues over the slate section with only slightly retarded velocity and jumps across the narrow opening and upon the continuation of the inclined floor below. The serious objection to this type of machine is the great loss due to the chipping of coal as it impinges against the upper edge of the continued floor below the opening. The loss is reported to be greater than that in the jig.

The second consists of a spiral floor descending and inclined inwardly toward its vertical axis. It depends for its operation upon the inward inclination of the floor toward the vertical axis tending to draw the slate in its retarded movement toward the axis, while the coal in its accelerated movement down the spiral incline is thrown from the floor by centrifugal force and is caught in a specially provided runway paralleling the spiral floor and spaced a little distance from it. This separating device is also very destructive to the coal as each and every piece as it leaves the spiral floor impinges against the outside of the runway. In quantity the loss is reported to be fully equal to that in the jig.

The third device consists of a moving floor inclined forwardly and transversely. The motion of the floor is upward on the transverse inclination. Both inclinations are adjustable. The material travels across the floor on its longitudinal inclination. The upwardly moving floor removes the impurities laterally from the forwardly moving stream. The coal slides upon the moving floor and across it without any impact. The loss sustained in this separator is less than one-half of one per cent. This machine is the only one that does not create material loss by attrition or chipping.

The tendency in the practice of to-day is to use, as extensively as possible, the machines that do not create loss, therewith turning to the pocket ready for market from 60 to 80 per cent. of the pure coal coming upon the machine, and without appreciable loss from chippings. This operation removes all of the cubical coal which gives unsatisfactory results in the jig. A second operation supplements it, retreating the tailings of the first, which removes the flat slate and heavy rock. This operation is again supplemented by a third, jigging, which removed the remaining slate in the balance of the coal. This three-stage process has the advantages of great elasticity and controllability.

The most important of all features in the entire process of anthracite preparation is to so handle the coal in transportation, screening, separation, conveying and loading as to retain the pieces of coal whether coming directly from the mine or from the crushing-rolls in their initial form without any loss in weight from abrasion or chipping, if at all possible to do so. The crushing-rolls must be of the type that will yield the very highest percentage of the prepared sizes, for in these sizes the values lie. These sizes are egg, through $3\frac{1}{4}$ and over $2\frac{5}{16}$ inch round mesh; stove, through $2\frac{5}{16}$ and over $1\frac{5}{8}$ inch mesh; and chestnut, through $1\frac{5}{8}$ and over $1\frac{1}{16}$ mesh.

The foregoing reference to the losses sustained in the process of jigging and in certain types of the frictional machines accentuates the importance of this feature of the process.

Great attention should be given to the avoidance of breakage in the transportation of the coal from one stage of the process of

preparation to the next, and finally its delivery into the deep pockets holding as much as 100 to 200 tons for each size. One of the most efficient means of doing this is by the spiral chute first introduced in 1896 in a breaker near Hazleton, Pa., by the writer. Another efficient device is the "waterfall-chute," first introduced in 1910 in the Lehigh Valley Coal Co.'s breakers, by Paul Sterling, Mechanical Engineer for that Company. It consists of a series of comparatively narrow floors in two vertical tiers, inclined toward each other and overlapping. Different dimensions are required for each size of coal. In its operation the coal flows from one floor upon the next floor below in the opposite tier, and so on, making the descent without material breakage. Either of these devices will deliver the coal to any vertical depth desired.

In like manner great savings can be effected with the exercise of due care in the design and construction of the loading devices. To illustrate the possible loss at this point in the process, it has been found by test that prepared sizes dropping 10 feet will depreciate 4 per cent. in fine chippings.

The preparation of bituminous and lignite coals must, in a general way, follow the same plan as that developed in the preparation of anthracite. This is manifestly so because the general formation of the beds and association of the impurities is the same. But because of the friability and soft nature of these coals the process has been modified to suit this inherent peculiarity. A close examination of the surface of the sized pieces of bituminous coal shows that the interlaminated bands of slate, although they may be as thin as india paper, protrude beyond the bands of coal, the coal having been worn or frayed away in the action of loading, dumping and screening. It is also observed that the very purest of pieces of bituminous coal have a greater angle of repose than even the least pure pieces of anthracite, showing that the slates are more siliceous. It is plain therefore that the jig, because of the friability of the coal, would not succeed within economic limits. On the other hand, because of the projection of the siliceous interlaminated bands of slate beyond the surface of the coal, the frictional machines have only a very limited range of efficiency. Any type of machine that produces impact will create serious disintegration and loss. Crushing the coal to half-inch mesh, and under, and treating it in a washer has proved very unsatisfactory and wasteful of the finest particles of coal, which have an equal value with the coarser particles in making coke, or for steam purposes and gas-producing. Many ingenious schemes have been brought out to accomplish the coveted end. One scheme has recently been brought forward whereby the coal is treated entirely in the dry state, without the use of any water, and which recovers, it is claimed, about 98 per cent. of the values of the coal.

The market value of any coal depends primarily upon the number of heat units per pound. In the anthracite field the standards of purity are expressed in percentages of slate in the coal, this being a convenient and reasonably accurate way of expressing the purity of the coal. It is made possible to express it in this way because of the hardness of the coal and the sized condition of the prepared product. In the bituminous field, because of the presence of so much fine material in the product, the chemical analysis determining the heat units and percentage of ash, sulfur, etc., must form the basis from which the value of the coal is determined.

In designing a preparation plant the recognized scientific principles underlying all of the methods of preparation together with the individual peculiarities of the coal to be treated should unquestionably form the basis for formulating the scheme. If these principles are consistently adhered to, a better preparation and more economic results will be obtained than can be obtained from trying to correct some inherent defects in the old methods, or to modify them beyond their fixed limits of efficiency.

HAZLETON, PA.

THE BEEHIVE COKE OVEN INDUSTRY OF THE UNITED STATES¹

By A. W. BELDEN²

The manufacture of coke in the United States, according to authenticated reports, was begun about 1817. From this date on, mention is made from time to time of the use of coke for metallurgical purposes, but the coke was made on the ground in pits or mounds and no record of any coke made in ovens can be found until the year of 1841 when two carpenters and a stone-mason formed a partnership for the building of two ovens and the manufacture and sale of coke. This plant was built in the famous Connellsville region, and although the business venture was unsuccessful, the coke proved useful for foundry purposes. This venture, together with experiments carried on during the next ten or fifteen years, fully demonstrated the value of this fuel, and production increased by leaps and bounds into the vast beehive coke oven industry which completely dominated the field until 1893, when the first coke oven plant for the recovery of by-products was introduced into this country.

The evolution of the modern beehive oven started as shown above and the process of coking in this type of oven has not materially changed, the modern increased efficiency being due in great measure to improvements in the ovens and the preparation of the coal before charging into the ovens.

BEEHIVE OVENS

The beehive oven, in its essential details, may be described as a circular vaulted fire-brick chamber constructed on a suitable foundation, with flat tile bottom, an opening in the top through which the coal is charged and the products of combustion escape, and an arched door at the bottom about three feet high, through which the air for combustion is admitted and the coke watered and drawn. The many variations and improvements since the ten-foot diameter oven of the carpenters and stone-mason of 1841 have led to the present standard beehive oven as shown in section, Fig. 1. The size of the door and the trunnel-head,

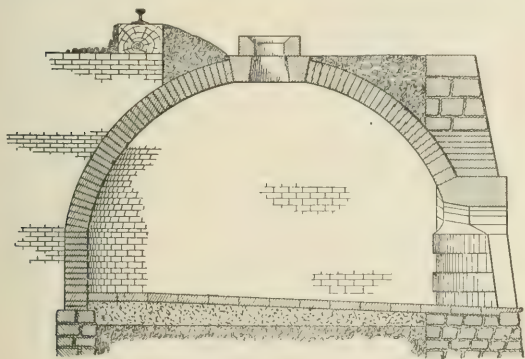


FIG. 1—BEEHIVE OVEN SECTION OF STANDARD TYPE,
12' DIAMETER 7' 6" HIGH

height of dome and diameter of oven vary in different localities, but the essential features are the same. The ovens are built in single rows called bank ovens or in double rows back to back or staggered. The coal, the amount of which is previously determined as the oven is to be burned 48, 72 or 96 hours, is charged into the oven from a larry car operated on a track above the ovens. The coal in falling into the oven forms a conical pile and is leveled by means of a scraper operated by hand. The door is bricked up to within two or three inches of the top

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912, by permission of the Director of the U. S. Bureau of Mines.

² Coke Expert at the Bureau of Mines Experiment Station, Pittsburgh.

and the oven left until the heat held by the bricks from preliminary heating, or the previous charge, raises the temperature to the point where the volatile matter, distilled from the coal, finally catches fire. The coking proceeds from the top downwards and the burning of the volatile to maintain the required heat is regulated by closing up the air opening as the amount of the volatile falls off. After the volatile has ceased to come off the process is finished. The door is then torn down, the coke watered on the inside of the oven by means of a spray of water and then drawn from the oven.

The beehive oven arranged for the mechanical drawing of coke differs from the above only in the width of the door and projecting iron jams at the sides of the door. Mechanical drawing of the beehive oven has been resorted to on account of the scarcity of labor and not from any increased efficiency resulting from the mechanical operation *per se*. There is reason to doubt if mechanical drawing shows any material reduction in the cost of operation when all the items are taken into consideration. It undoubtedly breaks up the coke more, producing

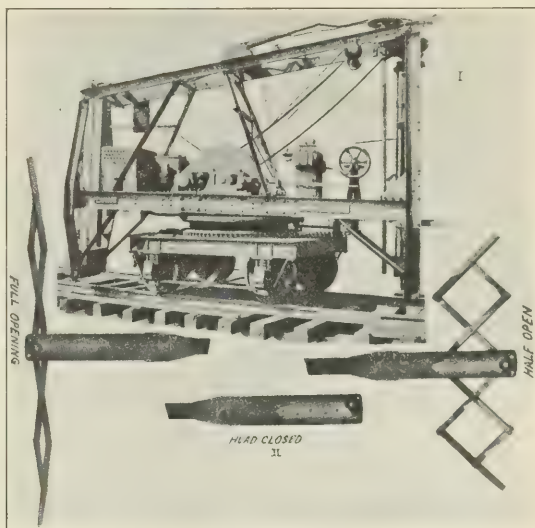


FIG. 2

a large percentage of breeze, but, on the other hand, it reduces the time of drawing very materially. The enlarged size of the door makes drafting more difficult and leads to much burned coke. The practice of watering far in advance of drawing and especially where the precaution of putting the lid on trunnel-head is not followed, leads to the rapid cooling of the oven and reduces the yield by increasing the length of time necessary for subsequent charges to ignite. This increases the time to burn the same size of charge or necessitates the reduction of the charge to burn ovens down on time.

Lately a patented machine for the mechanical leveling of coal in beehive ovens has been put on the market and is now in operation in the Connellsville coke region (Fig. 2). It runs on the larry track, uses the larry trolley, and operates through the trunnel-head. This machine gives evidence of proving its usefulness, not only by the elimination of hand labor, but by encouraging the proper leveling of the ovens, an operation too often neglected or considered of little importance. The proper leveling of the coal in any oven is a matter of great importance, and it is a source of regret that so little attention is paid to this feature of the process by the beehive operators throughout the country. With improper leveling, the different heights of

charge become coked to the bottom at different periods of time, thus exposing the top surface of the coke to the prolonged action of the air admitted for the completion of the process, with a resultant loss of coke, or if the process be stopped short of completion the coke from the higher portions exhibits black butts.

LONGITUDINAL OVENS

The decreasing efficiency and scarcity of labor and the increased cost of coking coal has led to experiments to reduce both of these factors, first by making the coking operation non-dependent on large numbers of laborers, and secondly by decreasing the cost of actual operation. From these experiments was evolved, in 1906, the longitudinal oven (a modification of the old Belgian type), with its mechanical devices for leveling, pushing and loading of coke. Fig. 3 shows a section of this

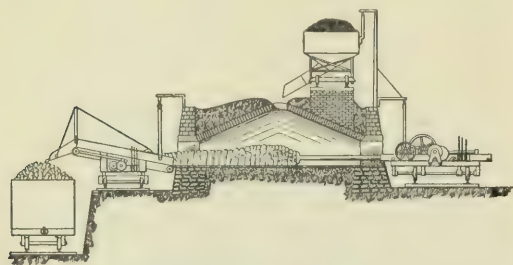


FIG. 3—LONGITUDINAL OVEN
SECTION SHOWING METHOD OF OPERATION

type of oven and the method of operation. In its essential details it may be described as a long, narrow, rectangular chamber generally somewhat larger at the discharging end, with sloping barrel roof approaching the center from both ends, a trunnel-head in center of roof, flat tile bottom and doors the whole width of the chamber at either end. These ovens are placed side by side forming a block and are charged as in beehive practice, from a larry running on a track supported on the ovens. The oven is drafted from both ends, after the method of the beehive oven, and the coke, after being watered on the inside of the oven, is pushed out by means of a pusher, devised for the purpose, onto a traveling conveyor, which transfers it to cars, screening being more or less fully accomplished during the passage of the coke along the conveyor. During the last three years this type of oven has come into prominence, especially in the Lower Connellsville region, and many claims are made for it in regard to increased yield, better product, lower cost of production, etc., but judgment must be withheld until these ovens have been in use for a longer period and prove their worth by actual service.

BEEHIVE OVEN WITH ARRANGEMENT FOR UTILIZING WASTE HEAT OF GASES

Waste heat from beehive ovens is utilized at some few plants in this country for the generation of steam. The ovens, either bank or double-row, are provided with a tunnel, built in case of the bank ovens directly behind, and the double-row between the rows, and extending the whole length of the ovens to be used for this purpose. From each oven a flue is provided leading from the oven to the tunnel and so arranged that it can be dampered off. This flue is placed in the crown of the oven above the height to which the coal is charged. Numerous schemes for placing the flues leading from the oven to the main flue have been tried. The usual practice is a short straight one from the oven direct to the tunnel. At the boiler end a large stack is placed to cause proper draft. In operation the regular trunnel-head is covered and kept closed, the gases passing through the flue into the tunnel instead of into the open air as in the case

of the ordinary beehive practice. The waste heat passes along the tunnel in the direction of the draft chimney and through the boiler setting before passing out of the stack. The temperature in these flues is very high (around 2700° F.) and the building of flues to withstand this heat is a matter of much consequence. The temperature of the gases at the boiler approximates 2000° F., and the gases are sufficient in amount to generate from 12 to 20 horse power per oven. The ovens burn hotter under these conditions, due to the better draft on the ovens than when burning into the air.

BEEHIVE COKING IN THE SEVERAL COAL FIELDS OF THE UNITED STATES

Beehive coke is produced in five of the seven great coal fields of the United States: Appalachian field in Pennsylvania, Virginia, West Virginia, Ohio, Tennessee, Georgia, Alabama and Eastern Kentucky; the Eastern Interior field in Illinois, Indiana and Western Kentucky; the Western Interior field in Kansas, Missouri and Oklahoma; the Rocky-Mountain field in Colorado, Montana, Utah and New Mexico; and the Pacific Coast field in Washington.

Pennsylvania has, from the beginning of coke-making in the United States, maintained the supremacy as to production, and the beehive oven coke from the Connellsville region is still considered the standard coke of the country. All other cokes from whatever section of the country are judged by comparison with this standard. The coal from this region, with approximately thirty-one per cent. of volatile matter, seems to contain just the proper amount and composition of this volatile and to be given off at the proper temperature and time to produce a maximum yield of coke with a minimum loss of fixed carbon during the process. Practically all the coal in this region is mined for the production of coke and is charged into the ovens without any special preparation whatever. About fourteen per cent. of the coal from other coking regions of the State is washed before coking, and the coke produced is of varying purity and physical structure. The table herewith shows the range of composition of the Pennsylvania cokes:

	PERCENTAGES
Moisture.....	0.23 to 0.91
Volatile matter.....	0.29 to 2.26
Fixed carbon.....	92.53 to 80.84
Ash.....	6.95 to 15.99
Sulfur.....	0.81 to 1.87

West Virginia coal is of exceptional purity and the coking industry, although second in production, is mainly as an incident to the furnishing of steam and domestic coal. More than sixty per cent. of the coal charged into the beehive ovens is slack and less than ten per cent. of it is washed. At those plants where proper attention is given to preparation of the coal and subsequent operation of the ovens themselves, a coke of superior chemical and physical properties is produced. The quality of the greater amount of West Virginia cokes is exceptionally good, but a wide variation is still to be found in the chemical composition of the cokes of this State as the following range shows:

	PERCENTAGES
Moisture.....	0.07 to 0.60
Volatile matter.....	0.46 to 2.35
Fixed carbon.....	95.47 to 84.09
Ash.....	4.00 to 12.96
Sulfur.....	0.53 to 2.26

The coke produced in Virginia is from coal in the southwestern part of the State and is all from unwashed coal. In chemical and physical properties it resembles the cokes from southern West Virginia.

The cokes from the southern part of the Appalachian field, comprising the States of Tennessee, Georgia, Alabama and eastern Kentucky, are, for the most part, made from washed

coal, the quality of coke is poorer and the ash and sulfur are high. The average ash is in the neighborhood of 14 or 15 per cent., and often running up to 16 and 18 per cent. where proper attention is not paid to preparation and coking. The Birmingham district of Alabama produces a fairly large amount of good beehive coke, with an ash content averaging 11 per cent., but such coke is the exception and not the rule.

Range of composition of above coke:

	PERCENTAGES
Moisture.....	0.75 to 1.34
Volatile matter.....	0.75 to 1.95
Fixed carbon.....	91.20 to 77.81
Ash.....	7.30 to 18.90
Sulfur.....	0.58 to 1.77

Beehive coking operations in the States of Illinois and Indiana are practically at a standstill. A few ovens for experimental purposes have been built in these States and have demonstrated the practicability of producing coke from some of these coals. The coking possibilities of Illinois and Indiana coals is confined to small areas, and beehive operations will hardly be established in these fields.

Kansas, Missouri and Oklahoma have had poor success in the production of coke and the total output from these States is very small.

Practically all the coke from the States of Colorado and New Mexico is made from coal previously washed and crushed before charging into the ovens. A plant of 350 beehive ovens of concrete construction is one of the novelties of this region. The ovens proper are of the ordinary beehive type, 13 feet in diameter and 7½ feet in height, constructed of firebrick and tile. The ring walls and wharf walls are of plain concrete, the battery walls and larry track columns of reinforced concrete. The yield of coke is reported above the average for the region and is believed to be due, in great measure, to the concrete construction which prevents the entrance of excess air so common in cracks developed in ordinary beehive construction. For details of this plant the reader is referred to *Mines and Minerals*, February, 1910, pages 429 to 432. At another plant in this region the ovens are provided with underflues which convey the gases from the coal under the oven bottom to a large flue, back of the ovens, which carries it to the power-house. This power plant furnishes all the power for operation of the mines, for ventilation, electric haulage, coal washing and crushing, and steam heat for the Company buildings and electric lighting for the entire community. The flues under the oven bottoms serve to hasten the coking and prevent black ends. The operation requires careful watching to prevent the coal from coking up from the bottom as well as down from the top. When the bottoms become too hot and this coking upwards does take place a distinct line of demarcation, where the two operations meet, is seen over the whole charge of coke.

The cokes of these States are uniformly low in sulfur, scarcely ever exceeding 0.75 per cent., but the ash is high, averaging 16 per cent.

The coals used for manufacture of coke in Utah are practically identical in character with those of western Colorado, but exhibit the surprising characteristic of losing their coking properties and becoming non-coking if kept in storage for any length of time.

Montana produces a very small amount of coke, all of which is used in copper smelters. Attention is called to the fact that the only restriction placed on the coke is that the ash content shall not exceed 20 per cent. This restriction is only complied with when the coal is washed. An average analysis of this coke shows 18.00 to 21.00 per cent. ash and over 2.00 per cent. sulfur.

Washington is the only State west of the Rocky Mountains that contains coking coal and the area within the State is small. All the coke is made from washed and crushed coal and is of fairly good quality. An average analysis of this coke follows:

	PERCENTAGES
Moisture.....	0.92
Volatile matter.....	1.50
Fixed carbon.....	79.58
Ash.....	18.00
Sulfur.....	0.52

BUREAU OF MINES EXPERIMENT STATION
PITTSBURGH

AMERICAN OIL SHALES¹

By CHAS. BASKERVILLE

In several communications by the author on the economic value of the oil shales of Canada,² it was shown that the beds of oil shale in New Brunswick are very extensive, that the principal by-product obtained on retorting (under suitable conditions), ammonium sulfate, will often more than bear the expense of mining and treatment, and that the crude oil obtained by retorting New Brunswick oil shale is essentially the same as the petroleum of the mid-continent field. The importance of these large deposits of fuel oil has been appreciated, for a strong company, The New Brunswick Shale Co., Ltd., capitalized at \$5,000,000, has been organized for their development. The formation of this Company and the doubtless early working of the New Brunswick shale deposits have aroused much interest in other parts of the Dominion, especially in New Foundland, Nova Scotia, and Ontario, where other oil shales occur, as well as in the United States.

The commercial success and tribulations of the shale oil companies now in operation in Scotland are well-known.³ The oil shales in the Worgan and Capertee Valleys, New South Wales, Australia, and at Autun and Buxiere les-Mines, France, are also being worked, while the Orepuki, New Zealand, and Camamu Basin, Brazil, oil shales were found, upon being worked, to be low-grade and to require high development charges. Although a company is being organized to acquire the oil shale properties situated near Ermelo in the Transvaal, the author is unaware of any large operations on the oil shale deposits of Spain, Austria-Hungary, Turkey, Tasmania, Mozambique, Natal, Italy, and the United States for the production of crude oil and ammonium sulfate. In this country, from 1854 to 1860, various bituminous materials were distilled for the production of illuminating oil by fifty-five "coal oil" companies, but the process followed was very crude and ammonium sulfate recovery was never attempted. Consequently, although many of the coals and other materials used were of high-grade,⁴ and merit investigation as to yield of oil, gas, and ammonium sulfate according to modern practice, it is not surprising that the discovery of petroleum paralyzed the industry. However, interest in these deposits and raw materials of more or less similar properties is awakening.

In the United States, oil shales⁵ occur in Kentucky; on the Humboldt River, opposite to Elko, Nevada; on the Big Blackfoot River and near Great Falls, Montana; and in the Cholame Valley, north of Parkfield, California. Some of these are of good quality, but none has been worked to any extent. It is likely, however, that the increasing demand for liquid fuel and ammonium sulfate may occasion a thorough investigation of these deposits. Some time ago the author examined a sample of oil shale from Montana. This shale was friable and blacy, being weathered; it yielded 41.5 pounds of ammonium sulfate and 6 gallons of crude oil per short ton.

Some carbonaceous shale is being used in the manufacture of

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² *Proc. Seventh Internat. Cong. Appl. Chem.*, 1910, Section IV, *Eng. Min. J.*, 88, 149-54, 195-99; *This Journal*, 1, No. 8 (1909).

³ See Ellis and Hamor, Canada Department of Mines, *Report 55*, Mines Branch, Ottawa, 1910.

⁴ Baskerville, *Eng. Min. J.*, 88, 151.

⁵ Reference is had here to shales which contain an oil-forming substance, kerogen, which gives rise to oily and tarry matters on destructive distillation; and not to oil-bearing shales, from which petroleum may be obtained by mechanical means.

paint in the United States, but in the processes employed the nitrogen present is not recovered.¹

The oil shale deposits of America constitute a fertilizer as well as a fuel resource of decided economic possibilities. How

ever, the methods by which these resources may be utilized with greatest profit require careful inquiry.

COLLEGE OF THE CITY OF NEW YORK

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE INDUSTRIAL FUTURE OF MAINE

On November 1, 1912, Arthur D. Little delivered an address on "The Relations of Chemistry to the Industries of Maine," before the Maine Section of the American Chemical Society in Bangor. After discussing the general relation of chemistry to the textile, lumber, paper and pulp industries, Dr. Little took up certain topics which seemed to be of special importance in considering Maine's industrial future. Among the most important of these were: The production of methyl alcohol from wood waste; the Maine peat deposits, and the great adaptability of this section to electrochemical manufacturing on account of the immense amount of water-power available. There can be no question about the great industrial future of Maine, and it is to be expected that Dr. Little's inspiring address will arouse the interest of manufacturers.

REINFORCED PLATINUM

B. D. Eldred has patented (U. S. Patent 1,043,576) the employment of one of the metals of the iron group as a backing to reinforce platinum. The platinum surface of the compound metal imparts resistance to the action of acids, while the iron-group metal used is of sufficiently high melting point to retain the property so useful in platinum, *viz.*, infusibility. The method of producing the compound metal is as follows: The metals are cleaned, and the base metal is heated through the platinum sheet by means of an oxygen or enriched-air flame to surface fusion of the base metal, then arresting the heating, as welding begins at that time. Another patent (U. S. Patent 1,043,577) pertains to the production of bimetallic plates by casting the ferrous metal, superheated, against the platinum; this is preferably accomplished in a U-shaped mold, casting the metal down through borax or a similar flux, and allowing it to rise in the other leg, against the platinum surfaces. The superheated metal of the iron group is produced by reduction of, say, iron oxide by aluminum. Eldred has also patented (U. S. Patent 1,043,579) the manufacture of spun ware from compound sheets, double-faced with platinum.

IRIDIUM IN AMERICAN PLACER PLATINUM

F. W. Horton (*Eng. Min. J.*, 94, No. 19, 873-5) points out that the unprecedented and ever-increasing demand for the various alloys of platinum and iridium, coupled with the limited production of both the component metals, has resulted in an almost uninterrupted rise in their price. The demand which has more than doubled the price of these metals and made iridium over three times as valuable as gold, has come largely from the jewelry trade. The superiority of "hard platinum"

as a setting for diamonds, pearls and light colored precious stones, both from an artistic standpoint and from that of durability and safeness of setting, together with the high price of the alloy, has made it very fashionable, and this firmly established demand greatly exceeds the supply.

Iridium not only makes a hard alloy with platinum, but it gives the alloy a greater electrical resistance and higher fusing point than that of pure platinum, and is consequently used in resistance coils and also in thermo-couples for the measurement of high temperatures. The proportion of iridium in the alloy ranges from 5 to 20 per cent., rarely exceeding the latter amount except in the case of special alloys where great hardness is desired. Alloys containing less than 10 per cent. of iridium are ductile and malleable. Where the alloy contains 30 per cent. or more iridium, it is no longer attacked by *aqua regia*. The properties of extreme hardness, high melting point, and insolubility render iridium particularly adapted to certain uses, as in the manufacture of knife edges for delicate balances, standard weights, pivots, contact points, etc. Pure iridium is, however, difficult to work because of its brittleness, and is, therefore, usually alloyed with a small percentage of platinum even when great hardness is desired. The natural alloy of iridium with osmium, iridosmine or osmiridium, is, on account of its great hardness, used for watch and compass bearings and for tipping fountain-pen points. (An ounce of iridium is sufficient for making about 7,500 pen-points.)

The iridium used in this country is obtained principally from Russian crude platinum, which generally contains from 1 to 3 per cent. of the metal. Similar small percentages of iridium are also obtained from the crude platinum which is imported from Colombia, and this amount is supplemented by an annual domestic production of 100 or 200 ounces. The total imports of "iridium and iridium in native combination with platinum metals" into the United States in 1911 amounted to 3905 ounces, valued at \$210,616; less than 3.2 per cent. as much iridium as platinum was imported.

It is quite generally known that a small percentage of iridium is usually found in the small quantities of crude platinum which are produced annually in the United States as a by-product of placer mining; but Horton calls attention to the high percentage of iridium associated with the crude platinum from certain districts in this country and the comparatively large amount in which the metal might perhaps be obtained if the potential sources of supply were thoroughly investigated. There is at least one considerable area, and probably two, in Trinity County, California, where the gravels contain approximately twice as much iridium as platinum; and in the Oroville, California, district, the crude platinum contains a considerable percentage of osmiridium. The richer gold placers along the Trinity River, within the area where platinum metals occur, are at present largely exhausted, and the few hundred ounces that are now produced annually as a by-product in gold mining go but a little way toward satisfying the domestic demand. However, Horton inquires: "Is there not a possibility that in these areas there are gravels rich enough in the metals of the platinum group to be worked successfully where the gravel could not be mined at a profit for gold alone, and this because the gravels of the region have been prospected only for gold and without

¹ The Nashville Carbon & Oil Company, of Nashville, Tenn., are producing a "natural carbon" paint ("Durbon") from shale; the raw material is heated in air-tight retorts, and from 8 to 10 gallons of crude oil are produced from 1 ton. Both the dark oil and the black residue are used. The Natural Carbon Paint Company, of Freeport, Ill., formerly mined carbonaceous shale both in Mt. Carroll and Eleroy, Ill.; this was distilled in special retorts, and black carbon pigment, shale oil, and gas were obtained as products. The shale oil was said to contain a large percentage of ichthylol, but it was not utilized, the manufacturers operating the plant having been only interested in the production of a pigment suitable for what was regarded as an anti-corrosive and steel protective paint. For two years, up to November 1, 1911, the plant was operated by a Chicago paint company.

reference to their content of the much more precious metals iridium, platinum, osmium, etc., and that gravels well worth mining, particularly at the present price of iridium and platinum, may have been passed over because they contained little or no gold?" This query applies with equal force to the alluvial deposits in the entire serpentine and peridotite areas of the coast range, in northern California and southern Oregon.

THE PURCHASE OF LIME FOR WATER PURIFICATION

Monfort (*Eng. News*, 68, No. 20, 889) points out that lime for water treatment is valuable in proportion to the percentage of water-soluble calcium oxide which it contains; but that its value is diminished disproportionately by the presence of magnesia, alumina, silica, and unburnt stone, although for certain purposes these materials may be harmless or nearly so. "Hydrated lime" has been used by numerous railroad and commercial softening plants, and in some smaller cities; but its relatively high cost, the difficulties encountered in feeding it on a large scale, and the abundance of dust liberated in handling it have limited its application. In most of the larger plants, quicklime is used, but Monfort states that the vagaries of the specifications for the purchase of this latter material are numerous. In his opinion, specifications for the purchase of lime should be based upon a single percentage guarantee; and bonus and penalty clauses introduced to guard against the loss incident to impurities should be in terms of the percentage of the contract price. The increment should be sufficiently large to provide an actual bonus and penalty for variations in the quality of the lime delivered, and should be based upon the source and quality of the lime available. Well-burned lime (the "overburned" lime of the trade) suffers slight deterioration in transit, especially if covered with paper. Methods of sampling and analysis should be described in the specifications.

THE EFFECT OF BOILER SCALE

Power (36, No. 18, 634) reports that recent tests made by the Engineering Department of the University of Illinois show the possibility of heat loss from mineral incrustations inside of boilers varying in thickness from $1/30$ to $1/16$ inch. Experiments gave the following results:

Character of scale	Thickness Inch	Composition	Loss Per cent.
Hard	$1/30$	Mostly carbonates	9.4
Soft	$1/32$	Mostly carbonates	7.2
Hard	$1/32$	Mostly carbonates	8.5
Soft	$1/25$	Mostly carbonates	8.0
Hard	$1/20$	Mostly sulfates	9.3
Hard	$1/20$	Mostly sulfates	11.1
Soft	$1/16$	Mostly sulfates	10.8
Soft	$1/16$	Mostly carbonates	11.0
Soft	$1/16$	Mostly carbonates	12.4

The results illustrate how good evaporative results may be handicapped, not only 12 per cent., but even more, by allowing incrustations to increase beyond the $1/16$ inch thickness.

NITRIC ACID FROM COKE-OVEN GASES

The *Zeitschrift für angewandte Chemie*, 25, 2309, reports that a company, capitalized at 1 million marks, has been organized in Heringen bei Hamm for the manufacture of nitric acid from nitrogen. Particular attention will be paid to the utilization of gases from coke-ovens, and a plant is to be established in connection with the coke plant of Zeche de Wendel in Hayingen.

THE ELECTROTECHNICAL PRODUCTION OF AMMONIA

The *Zeitschrift für angewandte Chemie* (25, 2258) states that two concerns are at present engaged in the manufacture of ammonia in Norway: one of these is Norwegian ("Det Norske Aktieselskab for Elektrokemisk Industri") and the other French

("Société Générale des Nitrures"). A third company, "Det Norske Nitritaktieselskab," has just been organized, and a plant is being erected in Arendal which is to run on an experimental scale in 1913 and is to be put into full working operation in 1914. The 25,000 horse-power necessary is to be obtained from Arendal water-power and a production of 40,000 tons per year is contemplated. An investment of 15,000,000 francs is assured, mostly French and partly Norwegian capital. The originators of this project are Messrs. Bernheim and Badin, of Paris, and S. Eyde, of Christiania; the two first mentioned control the "Société Générale des Nitrures." The last mentioned French company is manufacturing ammonia by a French electrochemical process; the ammonia produced is used in the preparation of "kalksalt peter." Ammonia is used in larger quantities at the Notodden factories, where, until recently, the ammonia was obtained from Germany and England, but is now being produced by the Serpek process.

A factory for the utilization of atmospheric nitrogen is proposed to be erected in Finland. It is said that suitable limestone and water power are available, and that, if the preliminary experiments are satisfactory, the necessary capital has been subscribed for a large company.

It may be mentioned here that during the last ten years or so the production of nitrites in Germany has been monopolized by a number of large lead works, which formed a syndicate. Now, owing to the growing production of "atmospheric nitrates" in Norway, Sweden, and Switzerland, which enables the producers to manufacture nitrite much cheaper than when sodium nitrate is used, the German manufacturers are no longer able to compete profitably and a number of firms have discontinued this branch of their business, in consequence of which the syndicate has been dissolved.

THE PRODUCTION OF CALCIUM CARBIDE

In 1911, there were produced 18,000 tons of calcium carbide in Spain, 16,000 tons of which were consumed there and 2,000 tons exported. In Italy, 28,000 tons were manufactured, 23,000 tons of which were used and 5,000 tons exported. In Germany, however, only 7,500 tons were produced, and 36,230 tons were consumed, 29,230 tons of which were imported from other countries. Norway and Sweden exported 48,000 tons, Switzerland 26,000 tons, and the United States 13,000 tons. France produced 32,000 tons, all of which was consumed in that country. The production of England was small.

At Odda, in Norway, more than 30,000 tons of calcium carbide are manufactured annually; at this place, nitrolim works have been erected near the carbide plant. The production of carbide is to be attempted near Sydney, Australia; large quantities of the material are now imported from the United States and Sweden.

Two concerns control the carbide output in the United States. Acetylene is now supplied in compressed form in cylinders at a pressure of about 120 pounds to the square inch. Acetone, which dissolves 25 volumes of the gas per atmosphere at 60° F., is widely employed; generally, about 40 per cent. of the tank volume is filled with the liquid and an absorbing material, as asbestos. Large quantities of acetylene are produced at Joliet, Ill., for steel-cutting and welding.

THE JAPANESE WINDOW GLASS INDUSTRY

Window glass is manufactured in Japan at Amagasaki, the factory at which place is under the direction of a Belgian expert. The glass is hand-blown, in which operation certain Japanese are very efficient, and mechanical blowers have never been tried. The glass produced is much too green and is deficient in transparency; it is marketed only in the form of small sheets, and is accordingly most used for half-sized window panes and

small pictures. The sand which is used runs high in calcium carbonate, the other components of the batch are imported from Germany. The Amagasaki factory commenced operations with four furnaces, and was run at a loss, but now, with an increase of two more tanks, there is a profit in the manufacture.

While Japanese window glass does not offer any serious competition to foreign-made glass at home, considerable quantities being still imported, yet the Japanese industry is making a strong effort to get into the Chinese market. However, the quality is low, the packing faulty, and the loss from breakage and poor glass is so great as to overcome any margin of price in favor of the Japanese product. The bulk of the Chinese trade is held by Belgium, the United States having no part in the supply. The use of window glass in China is still restricted to parts of the country where winter must be resisted, and among the wealthy and foreign inhabitants.

PRECAUTIONS IN HANDLING COMPRESSED GASES

The French Minister of Commerce has submitted to a commission the question of precautions to be taken with cylinders containing compressed gases. The following rules are laid down (*J. du Four Elec.*, November 1, 1912):

The cylinder holding compressed gases for autogenous welding or for cutting metals should not be used in works where there are floors above containing people. Before being used, each cylinder should be placed in a trench of which the sides are protected by battens of wood, and only the neck of the cylinder should protrude above the surface of the ground. The cylinder should be located at least 5 meters from any fire, etc. Every cylinder should bear a legible indication of the date when it was placed in service, the pressure to which it was submitted at the last test, and the date of the test. No lubricants other than glycerin or soapy water shall be employed for greasing the valve. No application of heat shall be employed in facilitating the opening of the valve, even though this opening proves to be difficult. In employing oxy-hydrogen gas for welding, there should always be a mixer between the bottles and the flame, and there should always be a distance of at least 3 meters between the neck of the flask and the neighborhood where the flame is to be employed.

THETA TUBING

"Theta" tubing, invented by H. W. Jacobs, and manufactured in Atchison, Kansas, is a special shaped tube which combines maximum strength with minimum weight. It is said to possess very desirable qualities for bicycle and motorcycle frames, aeroplane frames, and other light vehicles which require more strength than the present round tubing affords. "Theta" tubing is so-called because its cross-sectioned shape resembles the Greek letter θ . The tubes are made of sheet alloy steel, which, when oil-treated has its tensile strength increased by 60 to 75 per cent. Two sheets are bent over mandrels to about the required shape and then welded together; the surfaces are then ground on an emery wheel, making the welded portion as smooth as the rest of the tube. A machine is being devised to roll the material out in flat sheets and another for welding the tubing.

THE PRODUCTION OF CAOUTCHOUC

The Caoutchouc Exchange estimates the world's production in 1911 at about 98,000 tons, out of which at least 2,500 tons were taken on account of direct sale. The fall in prices was due to the greater production of Para; but, on the other hand, while the conditions of shipping had been unfavorable the last recorded year and considerable quantities of raw caoutchouc were held back, this was put on the market in 1912. The world's consumption undoubtedly increased in 1912 over

the others; and if such a relative increase were to continue, then, states the *Chemiker Zeitung* 136, 1334), there would exist no doubts about the advisability of acquiring the great plantations in the next few years to come. The same authority predicts a constant fall in price. The English plantation companies have, as far as rentability is concerned, satisfactorily developed, and at the end of the year large dividends were declared.

The production from January to August, 1912, amounted to 21,733,661 pounds, as against 11,583,235 pounds for the same period in 1911, and 7,229,250 pounds in 1910. The increase in production in 1912 was about 88 per cent. over that of the other years, and in the month of August, 1912, alone, 3,655,535 pounds of caoutchouc were placed on the market. The Ceylon production was 7,961,509 pounds for the fiscal period in 1912, as compared with 3,570,627 pounds in 1911. It is worthy of attention that now, for the first time, the prices for Plantation Para are distinctly lower than those for raw Para, or "wild Para." The usual London quotations (converted to U. S. currency) for 1 pound lots follow:

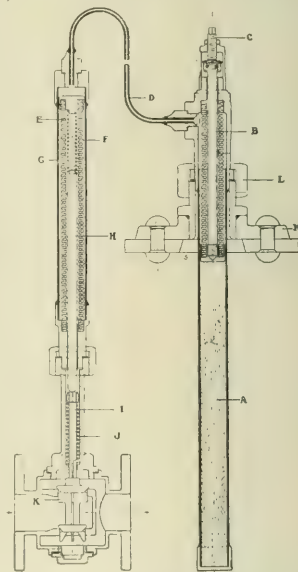
	Plantation para		Wild para		Scrap	
August, 1911	\$1 28 @	\$1 34	\$1 13 @	\$1 11	\$1 04 @	\$1 11
August, 1912	1 15 @	1 21	1 18 @	1 25	0.85 1/2 @	0.93
September, 1911	1 22 @	1 35 1/2	1 13 1/2 @	1 21	1 00 @	1 08
September, 1912	1 15 @	1 07	1 22 @	1 10	0.91 @	0.85

A WATER TEMPERATURE REGULATOR

The "Sarco" water temperature regulator uses as its actuating motive power the expansion of a sensitive liquid hermetically sealed within a chamber into which is inserted a flexible corrugated tube. In installing the apparatus, the thermostatic element is inserted into the tank or container, the temperature of which is to be regulated, and the valve is connected in the steam or hot water pipe, opening up or closing according to the temperature in the tank.

It is made of three principal parts: A, the thermostatic element which is inserted in the boiler or tank; G, the controller element; and, K, the valve. The sectional cut shows the construction.

The thermostatic element A is a tubular receptacle containing a heavy hydrocarbon oil into which is inserted a piece of corrugated copper tubing, the length of which is extended or reduced by turning the regulator head C. From this thermostatic element a piece of fine copper tubing D, passes to the controller G which also contains a piece of corrugated tubing capable of compression when an increase of temperature causes the surrounding liquid in A to expand. It will be observed that the thermostatic element A, the connecting copper tube D, and the controller G form one hermetically closed chamber. When temperature increases in A, the pressure increases and is transmitted to G, causing a compression of the copper tube F which forces out the piston I and tends to close the valve. Spiral springs E and J, operating in the opposite direction, tend to keep the valve open.



SOAP LYE AND SAPONIFICATION CRUDE GLYCERINS

The following standard specifications were drawn up by the British Executive Committee on Crude Glycerin Analysis, and approved at a general meeting of Crude Glycerin Makers, Buyers and Brokers, held in London on October 3, 1912 (*Chem. News*, 106, 242):

Soap Lyes Crude Glycerin

Analysis to be made in accordance with the International Standard Methods, 1911.

Glycerol.—The standard shall be 80 per cent. glycerol. Any crude glycerin tendered, which tests 81 per cent. glycerol or over, shall be paid for at a *pro rata* increase, calculated as from the standard of 80 per cent. Any crude glycerin which tests under 80 per cent. glycerol, but is 78 per cent. or over, shall be subject to a reduction of one and a half times the shortage, calculated at *pro rata* price as from 80 per cent. If the test falls below 78 per cent., the buyer shall have the right of rejection.

Ash.—The standard shall be 10 per cent. In the event of the percentage of ash exceeding 10 per cent., but not exceeding 10.5 per cent., a percentage deduction shall be made for the excess calculated as from 10 per cent. at *pro rata* price; and if the percentage of ash exceeds 10.5 per cent., but does not exceed 11 per cent., an additional percentage deduction shall be made equal to double the amount in excess of 10.5 per cent. If the amount of ash exceeds 11 per cent., the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 3 per cent. A percentage deduction shall be made of three times the amount in excess of the standard of 3 per cent., calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 3.75 per cent.

Saponification Crude Glycerin

Analysis to be made in accordance with the International Standard Methods, 1911.

Glycerol.—The standard shall be 88 per cent. Any crude glycerin tendered, which tests 89 per cent. or over, shall be paid for at a *pro rata* increase, calculated as from the standard of 88 per cent. Any crude glycerin which tests under 88 per cent., but is 86 per cent. or over, shall be subject to a reduction of one and a half times the shortage, calculated at *pro rata* price as from 88 per cent. If the test falls below 86 per cent., the buyer shall have the right of rejection.

Ash.—The standard shall be 0.5 per cent. In the event of the percentage of ash exceeding 0.5 per cent., but not exceeding 2.0 per cent., a percentage deduction shall be made equal to double the amount in excess of 0.5 per cent. If the amount of ash exceeds 2 per cent., the buyer shall have the right to reject the parcel.

Organic Residue.—The standard shall be 1 per cent. A percentage deduction shall be made of twice the amount in excess of the standard of 1 per cent., calculated at *pro rata* price. The buyer shall have the right to reject any parcel which tests over 2 per cent.

THE PRODUCTION AND EMPLOYMENT OF DEXTRIN

Parow (*Z. Spiritusind.*, 35, 507, 519) discusses the production of dextrin and its use. The yearly production of dextrin in Germany amounts to about 30,000 tons; in 1911, the quantity exported was 7,000 tons, although this was a poor year for potatoes. Dextrin is used as a substitute for gum acacia and gum arabic, in photography, as an excipient for dry extracts, for thickening mordants in printing fabrics, in the manufacture of paper, in printing tapestries, for preparing felt, in the manufacture of printing rolls and printers' balls, in the production of inks, etc.

Dextrin, which is produced from the starch of potatoes, corn, cassava and wheat, occurs in commerce in three forms: a powder

preserving the structure of the starch grains, a granular amorphous form, and a thick, milky liquid. The powdered form is obtained by heating starch meal alone or with 0.1 to 0.5 per cent. of acid. In manufacturing liquid dextrins and "crystal gum" some producers use roasted dextrin instead of boiling the starch with dilute acids, as the dry heating of starch gives less sugar than boiling with acids. When dry starch is roasted without the addition of acids, temperatures of from 100° to 250° C. are employed, depending upon the desired color and solubility. If the starch is "prepared," the roasting is conducted for 1 to 1½ or 2 hours at 100° to 125° C., depending upon whether the product is to be white or yellowish. The preparation of the starch consists in mixing with 0.25-0.20 per cent. of hydrochloric or nitric acid, and subsequent drying and pulverization. The acid, diluted with water, may be introduced into a drum in which the starch is kept well agitated. After breaking up any lumps, the product is stored for about one day to permit of thorough impregnation of the acid, and then well dried, ground, sifted, and fed to the roasting apparatus. If suitable mixing plant is employed, the starch meal can, however, be acidified in the dry state and roasted immediately. For example, in Blumenthal's apparatus, the meal is kept well agitated in a rotating drum, and the acid is injected in steam; in the method of Wulkan and Neumann, the whole amount of acid is first mixed with 6 to 8 per cent. of the starch, and this substantially dry mixture is then thoroughly mixed with the rest of the starch; Fielding completely dries the starch at 70° to 80° C. before adding the acid; and Uhland acidifies undried starch by allowing it, in the form of very fine flakes, to fall down a shaft into which the acid is injected in spray form, the product being again well mixed and dried. An easy control of the temperature is of vital importance, and is best attained by using roasting pans heated by oil, air or steam. In the production of white dextrin, the product should be cooled very rapidly, and apparatus for this purpose has been invented by Uhland. In a process devised by Pieper in 1894 a current of ozonized air is conducted through the roasting apparatus while the starch is being heated; and in Harweg's process the starch powder, moistened with a salt solution, is exposed to an electric current. "Crystal gum," or "Arabin," is made by dissolving slightly darkened dextrin, obtained by roasting, in hot water, decolorizing with animal charcoal, filtering, evaporating to dryness, and grinding. Commercial dextrin generally contains 10 to 12 per cent. of moisture, 5 per cent. of dextrose, and 0.2 per cent. of ash; it possesses an acidity corresponding to 3 cc. N/1 sodium hydroxide per 100 grams.

SOME ASPECTS OF THE FRENCH TURPENTINE INDUSTRY

An account of some aspects of the resin and wood-pulp industries of France and the United States is given by J. F. Briggs in *The Chemical World*, 1, No. 11, 369, from which the following material relating to the French turpentine industry is taken.

The French turpentine industry is confined to a triangular district called the "Landes," about 3,500,000 acres in extent, with Bordeaux as its principal town. About half this area, 1,750,000 acres, is forest-planted with the maritime pine, and the yield of crude turpentine is about 100,000 tons annually. In the United States, forests of long-leaf pine (*P. palustris*) and of certain other varieties occupy a strip about 125 miles wide along the coast of the Atlantic and Gulf of Mexico, extending on both sides of Florida to Virginia in the north and Texas in the west. The forest districts represent about 70,000,000 acres, a considerable portion of which has already been denuded by destructive exploitation. The annual production of the American forests is about 500,000 tons of crude turpentine. Until comparatively recently, these two countries were the only sources of resin products in the world, but small areas in other parts, notably Spain and Portugal, now account for possibly some 30,000 tons more.

The crude oleoresin, the "gemme," as it is called in the "Landes," exudes in the warm season (from March to October) from an incision made in the trunk. Kept open by the removal of a thin slice every week, this incision—the "carre"—rises gradually up the trunk until it reaches, after five years' working, a height of four yards or so. The tree is then left to recover for two or three years, after which time a fresh *carre* is made at another point of the base. The tree is thus tapped for about forty years, after which it is "bled to death" (several *carres* being worked simultaneously) before being felled for lumber purposes. In the "Landes" district strict arrangements are carried out for replanting the forest, so that the resin production of the district is maintained. In the United States this conservative system has not been followed, it having been the custom to tap the trees "to death" from the beginning, and every plot which was subjected to tapping was practically destroyed after four years' working, without any systematic steps being taken to ensure its re-establishment. Recently, however, this wholesale denudation has attracted public attention, and a better system of exploitation may be expected to result.

From the top of the *carre* the drops of *gemme*, as they exude from the resin ducts of the tree, run down into a receiver. In France, in former times, and in America, until quite recently, the receiver was merely a hole hollowed out of the trunk at the base of the *carre*. The irrationality of this method has, however, been recognized, and the general procedure now is to hang an earthenware or metal pot below the point where the resin is exuding. The contents of the pots are transferred about once a month into casks which, when filled, are taken to the distilleries. There the *gemme* undergoes two processes: first, a fusion for the separation of the oleoresin from the water and dirt; and, secondly, a distillation in presence of steam for the manufacture of the two commercial products, volatile oil of turpentine and non-volatile resin (rosin or colophony). The relative proportions of products of Bordeaux turpentine are 20 per cent. of oil, 70 per cent. of resin, and 10 per cent. of water and dirt.

Vèzes has done much work toward improving the quality of the products, not only in connection with the distillation, but also in connection with the collection of the crude material. It is recognized that the resin, both crude and in the course of manufacture, is a substance extremely sensitive to the oxidizing action of air and sunlight. This action adversely affects both the color of the product and its physical properties. A great improvement has been effected by reducing the period of exposure of the *gemme* during its stay in the incision, by raising the pot which receives the exudate at frequent intervals, so that the path traversed in its flow is as far as possible restricted, and by collecting the contents of the pots more frequently. By these alterations both the loss by evaporation of the oil and the coloration of the resin by oxidation are materially reduced.

THE DISPOSITION OF WASTE SULPHITE LIQUORS

Paper, November 20, 1912, p. 21, publishes some interesting correspondence pertaining to the utilization of the waste liquors of sulfite cellulose mills which recently appeared in the *Papier Zeitung*. The subject was occasioned by the publication in the *Frankfurter Zeitung* of a paper in which the problem of the disposition of the waste liquors of industrial plants in general was touched upon; this paper, in which the question of waste sulfite liquor was referred to as particularly urgent, was substantially as follows:

The utilization or unobjectionable disposition of the waste lyes of industrial plants has always been classed with the most important technical problems. At present, this question has become particularly pressing for cellulose plants working according to the sulfite process. The waste liquors of these establishments contain, in addition to sulfurous acid, about 10

per cent. of woodpulp in suspension which has been simply allowed to run off with the waste water. In consequence of the sulfurous acid, the lye is biologically detrimental to water courses, and has given rise to numerous complaints and claims for damages. In addition, the air in the vicinity of the mills has been badly contaminated. As a remedy, it was sought to utilize the waste liquors, useless for cellulose manufacturing, for other purposes, and, so far, two methods have been adopted. The process employed in Sweden is perhaps the most rational. Here the waste liquors are used in the production of alcohol, being first treated with acid and at the same time aerated to promote oxidation; the liquid is then neutralized, fermentation is started, and finally the alcohol produced is distilled off. This process is not economical in Germany. Recently, the idea of obtaining a solid product by the evaporation of the liquor was proposed, and this is effected by a process patented by Trainer. A plant on the Rhine is operating this process and produces from the waste lyes what is known as "Zellpech." This product, when solid, is a transparent, resin-like substance, containing about 11 per cent. of water, 15 per cent. of ash, and 36 per cent. of carbon; exposed to heat, it does not soften, but decomposes and finally burns without smoke; it is perfectly soluble in water and the solution has adhesive properties. It can be employed as a binder in coal or metal briquetting, for which purpose it is said to have advantages over coal-tar pitch. At a plant in Bruckhausen, 180,000 tons of blast-furnace dust are said to be daily transformed into briquettes with the aid of cellulose pitch. Finally, the lye, concentrated to a syrupy consistency, is an excellent medium for laying road dust. Ten kilos of lye, on evaporation, are said to yield 1 kilogram of pitch, so that it is claimed at least 500,000 tons of pitch can be produced annually in Germany alone.

To the preceding paper the Association of German Cellulose Manufacturers sent a reply, which follows in abstract:

"Where the waste liquors from cellulose plants are sufficiently diluted, biological damage in water-courses is not caused; it is only where mills are located on inadequate streams that such troubles have occurred. The 'Zellpech' plant in Rhineland has been able to utilize its waste liquor in making briquette material because it was financed and supported by capitalists who were particularly interested in securing an outlet for the coal and ore waste by the employment of the waste liquor as a binder. The geographical location of the Rhenish works is particularly favorable; the cellulose pitch can be marketed in mines in the immediate vicinity, so that transportation charges play hardly any part. The utilization of all the cellulose waste liquors produced in Germany for the production of pitch would, moreover, be an impossibility, as the necessary outlet would be lacking. The idea of producing a solid product from spent sulfite cellulose liquor by evaporation is not of recent origin, and experiments in this direction date back many years."

In a later communication to the *Papier Zeitung*, a paper-maker says:

"The cellulose pitch, so enthusiastically praised in the *Frankfurter Zeitung*, contains 15 per cent. in place of about 10 per cent. of ash. The pitch is exceedingly hygroscopic and, in spite of its paper wrapping, must be stored dry, or it loses its crispness and deliquesces. It must be finely ground for commercial briquetting. Damp, tough and no longer crisp the pitch causes trouble in the grinding, and, as the process of briquetting with hard cellulose pitch is patented, a license must be paid for its use.

"For briquetting blast furnace charging dust, zellpech is used by but one furnace and the results are kept as secret as possible. Most furnaces find that they can briquet cheaper with the concentrated thick liquor and do not favor the use of the cellulose pitch.

"For coal dust briquetting the cellulose pitch is practically

unavailable because of its high percentage of ash. It crumbles before burning and about two-thirds of the heating value of the briquette is lost in unconsumed substance in the ash. Shortly before his death, Trainer, who is freely quoted by the *Frankfurter Zeitung*, acknowledged that a good, combustible briquette could be made only with the aid of sulfite liquor freed from lime, an opinion that can only be confirmed.

"It is asserted that the coal briquettes made with thick spent liquor, gave no satisfactory results, even where made insoluble in water by preliminary heating.

"Attempts to use coke refuse or low-grade coal waste for briquetting with sulfite liquors, would involve heavy financial risk. It is said that even the best anthracite coal does not yield, with sulfite liquor, a commercially combustible product.

"That the briquettes are smokeless and do not soften under heat, is admitted and this may, in the future, prove a factor in coal-briquetting with lime-free lye. The weatherproof properties of the pitch praised in the *Frankfurter Zeitung* are of no consequence in relation to its combustible properties.

"The elimination of road dust has not so far been very successful, and if tar, so difficult of solution in water, is washed out in a comparatively short period, how much more quickly would the sticky, readily soluble sulfite liquor disappear. No large town can be named that, after the trials, has laid its road dust on a large scale with spent sulfite liquors."

NEW PRESSURE FILTERS

Bornett's pressure filters are being manufactured in several forms, with porous filter plates, for the filtration of liquids of all kinds, especially acid and alkaline solutions. It is claimed that they require but one man for the operation of a filter capable of dealing with 150 cubic meters of liquid leaving 30 tons of residue, and that in all cases the filtrate is clear.

The construction of the vertical type is shown in Fig. 1. A is the outside shell, or container, B is the filtering material, and C are filter plates. During filtration, A is hermetically closed and compressed air is forced in; the apparatus is not disturbed by air under high compression, and may be easily cleaned after the operation. The container is constructed of tin, lead, wood or clay, enclosed in a shell of cast iron or steel.

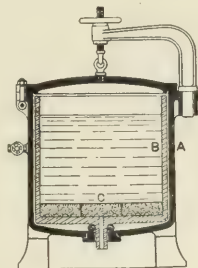


Fig. 1

The horizontal type is shown in Fig. 2. B is the cover of the

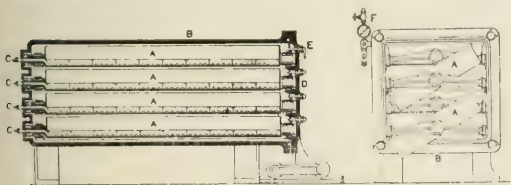


FIG. 2.

container and A the filter shell-plates arranged in a horizontal position. Underneath A, filter plates are placed in a position similar to that in the vertical filter.

THE PURIFICATION OF WATER BY "ALLOPHANOIDS"

Attention has already been directed to the purification of water by means of artificial zeolites (THIS JOURNAL, 4, No. 4). The Deutsche Filtercompagnie, G. m. b. H. (French Patent 440,351, February 19, 1912) now claim that "allophanoids" (the siliceous, non-crystallizable portion of volcanic rocks) may be used instead of zeolites in the purification of water,

particularly for the elimination of calcium and magnesium salts. It is said that "allophanoids" may be obtained by the elutriation of the powdered volcanic rocks by successive portions of water, they being lighter than the crystalline portions of the rocks.

"ELECTRIT"

"Electrit" is an abrasive made from aluminum oxide by fusing it in an electric furnace at a temperature of about 3,000° C. *The American Machinist*, 37, 24, states that its specific gravity is less than that of emery and corundum, but its hardness is considerably higher, being about 9.25 on the 10° sclerometers scale. The grain of "electrit" is almost amorphous; it is resistant under pressure and shock, and is tough and not brittle. "Electrit" grinding wheels are bound ceramically, are said to be proof against moisture and acids, and usable for wet or dry grinding.

THE UTILIZATION OF WASTE SODA LIQUORS

The *Société Commerciale des Crins* has a process for the utilization of waste lyes which have been used in treating vegetable fibers, especially cocoanut fiber, in the manufacture of hard and soft soaps. The waste lyes are filtered, then mixed with oils or fats in suitable proportions. It is claimed that the considerable amounts of dissolved resins present in the lye impart certain desirable properties to the resulting soap. Owing to the heavy cost of recovery, such lye is generally run to waste, so that the process presents the advantage of economy.

THE CASEIN INDUSTRY

Technical casein is discussed by Martin in *The Chemical World* for October, 1912.

The first firm to manufacture technical casein in Europe, and which performed most of the pioneer work in connection with this new industry, was a company known as "Casein Limited," founded by E. P. Carpenter. The firm consumes about 30,000 gallons of skim milk daily in the summer months, representing about 4 tons of casein daily. Their factories are situated at Tipperary in Ireland.

The starting point of the industry is skim milk. The casein is precipitated by various acids such as sulfuric, hydrochloric, acetic, lactic, and sulfurous (casein for different purposes is precipitated with different acids), washed, freed from traces of fat, and dried. The mother liquors and wash waters are worked for the milk sugar and milk albumin by partial neutralization, followed by low temperature concentration *in vacuo* and crystallization. The albumin may be separated by steaming, when it coagulates and separates on the surface of the sugar syrup. It is pressed to cakes and sold as a constituent of cattle foods. It is now more usually separated in a soluble form by a complicated and costly process and sold as a component for invalid foods under the names "Lactalbumin," "Milk albumin," etc. Refined milk sugar is used for children's foods, and for adding to various beers and stouts. The sugar, not being fermentable by ordinary yeast, may be added to the wort and remains in the finished stout to increase its "extract value."

Casein is largely used for sizing paper. It is dissolved in alkali solutions, and mixed into the paper pulp, when it forms an excellent binding agent for filling matter and pigments. The process is especially useful when the paper pulp has to be moulded or pressed into relief forms, as the casein size is very resistant to heat or moisture. When employed in certain special surfacing processes it produces extremely beautiful art papers. Some of the very best photographic papers are casein-sized, the papers being extremely resistant to heat and moisture, and thus will keep in the tropics.

More usually the casein solution merely supplements ordinary engine-sizing. The leather and textile industries also employ casein for "dressing" and "finishing" purposes.

Next in importance to its use as a "sizing agent" comes its use as a cold glue. Excellent glues are made merely by stirring up casein with distilled water and a little sodium bicarbonate, sometimes with the addition of shellac. In the woodworking trade casein glues threaten to displace ordinary gelatin glues because casein glues can be applied cold (so that all the trouble of melting the glue is avoided), can be made waterproof, and by their use certain delicate effects are attainable in veneering work which are impossible with gelatin glue, since the latter must be applied *hot* and is not waterproof. Several American firms are now producing these glues in large quantities.

When treated with certain chemicals, casein is converted into extremely tough, hard substances like bone or ivory, which can be kneaded and moulded when hot and when cold can be polished and worked. The best known of these products is *galalith*, which is made by treating casein with formaldehyde.

It forms a tough, white product, which can be colored or marbled when hot by stirring in dyes, soot, etc. It is now used for making piano keys, backs of brushes, imitation ivory articles, and especially as an insulating medium for electrical fittings.

Casein is used as a total or partial substitute for celluloid, but has the disadvantage that it cannot be produced in very thin, transparent sheets. Similar substances are produced by adding to a caustic soda solution of casein various chemicals such as sulfur, water glass, lime, sand, zinc and lead hydroxides, wood meal, cork dust, and so on. Such compositions are used for producing mouldings for picture frames, friezes, fancy articles, and toys. Casein is also used as a constituent of shoe polishes, etc., and an important and growing trade is the consumption of casein in foods, such as brain and nerve foods ("Viscem," "Sanatogen," and "Plasmon").

NOTES AND CORRESPONDENCE

OBITUARY—WILLIAM WILLARD DANIELLS

William Willard Daniells, emeritus professor of chemistry at the University of Wisconsin, died at the home of his son, Dr. Ralph P. Daniells, at Toledo, Ohio, on October 12th, at the age of 72 years. He graduated from Michigan Agricultural College in 1864, and then spent about two years in study with Wolcott Gibbs at the Lawrence Scientific School of Harvard University. Dr. Daniells came to the University of Wisconsin in 1868 as professor of agriculture. The following year analytical chemistry was also included in his department. In 1875 his chair was changed to chemistry and agriculture, and in 1880 he was elected professor of chemistry, the chair of chemistry having been established at that time. Dr. Daniells served not only as a teacher of chemistry, but also as a member of the State Board of Health, as State Analyst, as chemist to the State Geological and Natural History Survey, and in other advisory capacities. For several decades he was one of the very few reliable chemists of the middle west to whom the public could turn for expert services, and so his influence extended far beyond the university campus.

But while this scientific work together with the founding and upbuilding of a strong department of chemistry at the university stand to his credit, it is for his qualities as a man that Dr. Daniells will especially be remembered. He was an exceptionally strong, pure, lovable Christian character, who always stood for things that ought to be, and who exerted a quiet yet none the less potent influence for good upon his pupils, his colleagues, and all others with whom he came in contact. As a member of the American Chemical Society he always showed a live interest in fostering the work of the Society, and was instrumental in establishing the Wisconsin Section of the Society.

L. KAHLBERG

THE PRESENT STATUS OF THE WINDOW GLASS INDUSTRY

The total number of hand-operating window glass plants in the United States is 46, but many of these may not be operated throughout the entire year. On October 15, 1912, about 500 hand-operated pots were put into operation, and on November 1, 1912, the number was increased to approximately 989. This statement refers to factories located in Ohio, Indiana, Pennsylvania and West Virginia; in other sections of the country a possible total of 300 pots can operate if fuel and men are obtainable. The following is a list of the hand-operating plants:

PENNSYLVANIA FACTORIES¹

NAME	LOCATION	POTS
Allegany Window Glass Co.	Port Allegany	24
American French Belgian Co.	Dubois	30
Brookville Glass & Tile Co.	Brookville	30
Empire Glass Co.	Shinglehouse	30
Eldred Window Glass Co.	Punkstutawney	36
Federated Window Glass Co.	Point Marion	36
Jeannette Window Glass Co.	Point Marion	60
Masontown Window Glass Co.	Masontown	30
New Bethlehem Window Glass Co.	New Bethlehem	30
Point Marion Window Glass Co.	Guyaux	24
		330

WEST VIRGINIA FACTORIES

Banner Window Glass Co.	S. Charleston	18
Clarksburg Glass Co.	Adamston	33
Crescent Window Glass Co.	Weston	48
Dominion Window Glass Co.	Grafton	36
Dunkirk Window Glass Co.	S. Charleston	36
Doddridge Window Glass Co.	W. Union	24
Equitable Window Glass Co.	Buckhannon	30
Fairmont Window Glass Co.	Fairmont	30
Ideal Window Glass Co.	W. Union	24
Independent Glass Co.	Sistersville	24
Lafayette Window Glass Co.	Clarksburg	24
Modern Window Glass Co.	Salem	36
Patterson Glass Mfg. Co.	Cameron	13
Peerless Window Glass Co.	Clarksburg	24
Salem Co-operative Glass Co.	Salem	24
Tuna Glass Co.	Clarksburg	48
W. Fork Glass Co.	Clarksburg	30

502

OHIO FACTORIES

Buckeye Window Glass Co.	Columbus	27
Camp Glass Co.	Mt. Vernon	54
Case & Merry Co.	Maumee	30
Crystal Glass Co.	Pleasantville	24
Sandusky Glass Co.	Sandusky	30
Licking Window Glass Co.	Utica	72
Utica Glass Co.	Utica	48

285

KANSAS FACTORIES

Chanute Window Glass Co.	Chanute	30
Cheyenne Glass Co.	Caney	30
Caney Window Glass Co.	Caney	30
Fredonia Window Glass Co.	Fredonia	48
Kansas Window Glass Co.	Coffeyville	12

150

¹ These plants are rated by a unit pot which represents an output of 50 boxes of 50 square feet each per day. The writer is indebted to Mr. George B. Kimes, of Pittsburgh, Pa., for certain of the information used in this report.

OKLAHOMA FACTORIES

NAME	LOCATION	POTS
Baker Bros. Glass Co.....	Okmulgee.....	30
Coffeyville Window Glass Co.....	Okmulgee.....	54
Ponca City Glass Co.....	Ponca City.....	24
		108

TEXAS FACTORIES

Texas Window Glass Co.....	Texarkana.....	36
Wichita Falls Window Glass Co.....	Wichita Falls.....	36
		72

MISCELLANEOUS

Blackford Window Glass Co.....	Vincennes, Ind.....	30
Caddo Window Glass Co.....	Shreveport, La.....	54
		84

Grand total.....1,531 pots

The general resumption of the American Window Glass Company took place on October 26, 1912, although some of this Company's tanks did not start until November 1, 1912. About one-half of the sheet or window glass manufactured in the United States is produced by the American Window Glass Company, and in its production mechanical blowers, or "machines," are employed. The Lubbers' blowing machine eliminates skilled labor from the blowing departments, and this Company has at present 116 machines installed. Formerly, a glass-blower received about \$2,000.00 for nine months' work, while now the operator of a mechanical blower receives about \$600.00 for the same period; in addition to this, a machine is capable of producing more than 50 boxes of window glass in an eight-hour shift, whereas the hand-blower could produce only 60 boxes in 6 days. The cylinders obtained by the use of the improved Lubbers' blowing machine are from 25-28 feet in length and about 21 inches in diameter, although cylinders have been blown 44 feet long and 4 feet in diameter. It is now possible to produce plate glass in this manner, and it is reported that the American Window Glass Company will shortly enter the plate glass field.

The following factories are now operated by the American Window Glass Company:

LOCATION	POTS
Hartford City, Ind.....	104
Arnold, Pa.....	168
Bellevue, Pa.....	100
Jeannette, Pa.....	168
Kane, Pa.....	96
Monongahela City, Pa.....	48

In the process used by the American Company, the fluid glass is ladled from the furnace into the blowing pots, and is then covered, planed, and disclosed for the insertion and immersion of the head of the electrically controlled blowpipe, which is an iron tube 5 feet in length and 2 1/2 inches in diameter, except at its head where it is from 6 to 8 inches in diameter, and containing a central opening 2 inches in diameter. This preheated blowpipe head immersed in the molten glass is left long enough for the melt to adhere. A bubble is formed by the slow admission of compressed air, and an upward draw is then slowly made to form the straight neck of the cylinder. This neck, from 4 to 6 inches in length, is held stationary long enough to enable the importation of sufficient rigidity to it to proceed to the formation of the bell-shaped shoulder, or "bait," which determines the diameter of the cylinder to be drawn. The slowness of drawing, together with the viscosity of the glass in the pot, determines the length and diameter of the cylinder; and it may be said in general that the hotter the glass and the more rapid the drawing, the thinner the cylinder. The inflow of compressed air, as well as the upward movement of the blowpipe and adhering cylinder, are subject to the manipulation of the operator. A cylinder of any dimension is elongated from the cap to a length of 18 to 20 feet in 8 to 10 minutes, depending

upon the fluidity of the glass. When the cylinder has reached the desired height, it is cut by shears at the lower end, and deposited upon a "horse" for capping off, division, and cracking open. All of the latter operations are done by the aid of an electric heater, as in the tumbler, lamp chimney, and globe manufacturing industries.

The fire-clay blowing pots now in use are arranged in a row, about 14 feet distant from the melting furnace front. They are of peculiar construction, having a concavity centrally on both sides, about 4 inches deep and 30 inches in diameter, with shafts extending horizontally to pillar blocks and controlling mechanism, whereby the upper concaved side of the pot may be turned down and be cleaned by flame contact, and the other be refilled and utilized for blowing another cylinder.

Aside from the factories mentioned, there are a limited number of firms making machine glass in an experimental way; but these can hardly be considered a factor in the window glass industry. Some of these concerns follow.

NAME	LOCATION	POTS
Enterprise Glass Co.....	Sandusky, Ohio.....	36
Pittsburgh Plate Glass Co.....	Mt. Vernon, Ohio.....	48
Consolidated Window Glass Co.....	Hazlehurst, Pa.....	36
Smethport Glass Co.....	Smethport, Pa.....	36
W. R. Jones Glass Co.....	Morgantown, W. Va.....	

The long stoppage of the window glass plants has resulted in the cleaning up of manufacturers' stocks to an extent not approached before in 25 years. On October 12, 1912, there were in the warehouses of hand-plant operators 200,000 boxes, and stocks of the American Window Glass Co. were reported to be lower than they had been in years. A large glass brokerage company reported that stocks in the hands of the factories it represented amounted to only 160,000 boxes on October 8, 1912, of which more than one-half were small sizes and broken assortments. On October 12, 1912, brokerage stocks were being drawn upon at the rate of about 2,000 boxes per day.

An authority says:

"Those who have kept in touch with the operating capacity in former years know there can be no overproduction this year. The scale terminates May 29, 1913, and the combined hand plants cannot possibly produce more than three million boxes. Stocks in the hand factories are about seventy-five thousand boxes, which is the lowest in the memory of the writer.

"A firm and advancing market should be expected with regular and liberal purchases throughout the season. The customary dull period in January or February is not likely to be noticeable this year.

"Many factories have rebuilt their furnaces and flattening ovens and several have replaced their flattening equipment complete. New glass this year will be of a high standard both in quality and strength."

W. A. HAMOR

CENTENARY OF THE GAS INDUSTRY—COMMITTEE REPORT
Mr. A. D. Little, President American Chemical Society:

Your committee appointed December 29, 1911, to confer with the American Gas Institute and such bodies as may seem proper with a view to arranging some suitable celebration of the Centenary of the Gas Industry, reports that it performed the duty assigned it and that the centenary celebration designed was held at the Franklin Institute, Philadelphia, Pa., on April 18th and 19th under the auspices of the American Philosophical Society, the American Chemical Society and the American Gas Institute. Addresses were made by Dr. Charles E. Munroe on "By-Products in Gas Manufacture;" Hon. George B. Cortelyou on "The Commercial and Financial Aspects of the Gas Industry;" Mr. Alfred E. Forstall on "The Technic of Gas Manufacture;" Mr. Van Rensselaer Lansingh on "Gas as an Illuminant;" and Dr. Edward B. Rosa on "The Use of Gas for Heat and Power and the Testing of Gas." The sessions were presided over successively by Dr. W. W. Keen, President of the American Philo-

sophical Society, Mr. A. D. Little, President of the American Chemical Society, and Mr. J. M. Dodge, Vice President of the Franklin Institute. A luncheon was given to all present at the meetings by Mr. Samuel T. Bodine, President of the United Gas Improvement Co. A valuable and interesting loan collection of objects connected with the evolution of the Gas Industry was made by Mr. W. J. Serrill, Acting Secretary of the Technical Committee, and Dr. R. B. Owens, Secretary of the Franklin Institute, and placed on exhibition in the corridors of the building. An account of these objects and full reports of the addresses, with illustrations, have been published by the American Gas Institute in a volume entitled "Lectures delivered at the Centenary Celebration of the First Commercial Gas Company to Sell Gas as an Illuminant" (N. Y., 8vo., 174 pp., 1912). The addresses have been republished in the *Journal of the Franklin Institute*, and in the June number of that journal there appears an article by Mr. Walton Forstall on "The Centenary of the Introduction of Gas as an Illuminant" in which many interesting details regarding the centenary celebration are given, and in which the special propriety of holding the celebration at the Franklin Institute is set forth.

Independent of this celebration several sections of the American Chemical Society regarded the event of sufficient significance to warrant special recognition. The Pittsburgh Section held its meeting on April 5th when addresses were made by Dr. Charles E. Munroe on "The Gas Industry and Its Centenary," and by Dr. W. O. Snelling on "The Production of Liquid Petroleum Gas." The Syracuse Section held its meeting on March 15th when it was addressed by Dr. Charles E. Munroe on "The Gas Industry and Its Centenary." The Washington Section held its meeting on May 1st when it was addressed by Dr. Charles E. Munroe on "The Gas Centenary, Its Origin and Meaning." Mr. Walter R. Addicks, Vice-President, Consolidated Gas Co. of N. Y., on "Gas Appliances;" Mr. W. H. Gartley, Engineer of Works, U. G. I. Co., Philadelphia, on "Internal Operations of the Lowe Process;" Mr. E. G. Runyan, Inspector of Gas and Meters, Washington, D. C., on "Inspection of Gas and Meters;" and by Dr. W. O. Snelling on "Liquefied Natural Gas."

Numerous articles relative to this event have appeared in the scientific and technical press. As showing with what importance this event has been regarded, attention may be called to *The Leipziger Illustrirte Zeitung* which, on June 27th, published a 118-page supplement, styled *Gas-Jahrhundert-Nummer*, which is profusely illustrated and which contains articles relative to gas, gas appliances, coke and related topics from the pens of the principal experts in Germany. The brochure, published in August by the London Company, whose founding was celebrated, entitled *The Gas, Light and Coke Company*: an account of the progress of the Company from its incorporation by Royal Charter in the year 1812 to the present time, 1812-1912, is a splendid example of typography and book-making, in 92 pages with 45 illustrations. The engineering appendix is of special interest to chemists. It may be of value to note, from among other statistics most fully given in this book, that the capital of the Company in 1912 was £29,154,146. Gas sold in 1911 was 25,484,985,000 cubic feet. Number of workmen employed, 12,637. Miles of main, 2489. Area of district supplied, 125 square miles.

In addition to the gentlemen mentioned above, your Committee, on behalf of the Society, tenders thanks to Mr. E. C. Brown, Editor of the *Progressive Age*; Hon. Ira C. Copley, M. C., President of the American Gas Institute; the officers of the Franklin Institute; the officers of the United Gas Improvement Co.; and Mr. George G. Ramsdell, Secretary, American Gas Institute, for their very efficient aid in the carrying out of the wishes of this Society.

Very respectfully submitted,

CHARLES E. MUNROE, *Chairman*

E. G. LOVE

E. G. RUNYAN

PLATINUM THIEF

Fellow Chemists: The Chief Chemists of a large number of laboratories will recall having received about the first of November, 1912, a circular letter from the Secretary of the American Chemical Society, worded as follows:

PLATINUM THIEF: WARNING

Gentlemen: I am sending this letter to all corporate members of the American Chemical Society and to numerous other important firms using platinum in their laboratory work, in the hope that a platinum thief may be apprehended who has already successfully stolen, from nine laboratories, platinum to the value of several thousand dollars. He seems to have entered both college and industrial laboratories with success. His description as obtained from several is as follows:

Man, apparently of the Jewish race, about 40 years of age, with German accent. Height, 5 ft. 8 in. Weight, about 220 lbs. Peculiarly shaped head, bald, clean shaven, large short neck, heavy jaws, dark complexion, dark hair and eyebrows. Talks intelligently. Represents himself to be a book and magazine salesman or in search of employment for himself or friend.

If such an individual is found and suspected, interested parties who can identify him will be immediately informed upon the receipt of a telegram sent to this office.

Very truly yours,

CHARLES L. PARSONS, *Secy.*

This letter was sent out in response to a request and based upon information furnished by this laboratory. Great labor was entailed in the Secretary's office in preparing a list of reasonable proportions including the leading platinum users in the country and in issuing the letters. That the work in this office was well done is evidenced by the results.

On October 1st, the individual described in the circular letter made two public visits to this laboratory. The next morning a certain amount of platinum was found to have been stolen. Immediate correspondence with one of the leading platinum works elicited the above description, tallying with my own observation of the man, also a list of a number of laboratories in widely distant parts of the country from which it was thought platinum had been stolen by this man during the previous five months. All of this information was transmitted to Dr. Parsons.

On Nov. 10th, a dispatch from the Maryland Steel Company stated that a man answering the description in the circular letter had been arrested and would be held pending our identification. Later during the same day I personally identified the suspect, Leon Cohn, as he signs his name, and on the following day he was brought back into Pennsylvania by an officer, upon a warrant from this Company. Cohn's conduct at the plant and in the laboratories of the Maryland Steel Company was of a highly suspicious nature, though here as elsewhere, so far as ascertained, the facts are of a circumstantial nature.

It has been learned that depositions taken at other laboratories can not be used in the trial of Cohn upon prosecution by this Company. I have received a number of letters giving evidence proving in all moral certainty that the man under arrest is the criminal, who successfully stole platinum from so many laboratories. However, the evidence in no single case so far received is as conclusive as desired. The prisoner at first made distinct overtures towards confession but has since employed expert legal advice and intends to fight the case. It is likely to prove a difficult matter for this Company to obtain a conviction on the merits of our case alone.

It is believed that some other laboratory or laboratories will be able to furnish more direct evidence and should the present case fail we trust their companies would be willing to start a new prosecution. This man is too dangerous to release. Obtain one conviction and the others will speedily follow. Under the shadow of certain conviction we feel confident that the crim-

inal will make a complete confession, including the disclosure of the stolen platinum, a part, at least, of which probably may yet be recovered.

I will ask, therefore, that any laboratories (with which we have not corresponded already) which have lost platinum in the last year or so and can give a description or evidence concerning the suspected thief to communicate with me immediately. [A photograph of our prisoner will be sent for proper identification purposes.] Kindly give all important details. By this method of coöperation I trust that we may speedily develop a case resulting in the recovery of the large amount of platinum and in the punishment of the thief.

R. J. WYSOR, *Chief Chemist*

P. S. December 23rd. The above article was intended for publication in the December issue of *THIS JOURNAL*, but it was sent in too late for that number. Very recently fresh evidence, which will be applicable to our own case, has been secured by this Company, and we are now confident that a conviction will be obtained. The case comes up for trial in February. However, it will be wise to have the essential evidence in all the cases in our possession before that time.

R. J. W.

BETHLEHEM STEEL CO.
S. BETHLEHEM, PA.

ARKOSITE

Arkosite is the trade name given to a new pigment and filler which may be found to possess valuable and important uses in many lines of industry. It is a true asphaltite, no foreign matter being associated with it, and it combines many technical properties. It is chemically inert and neutral, non-catalytic, non-hygroscopic, non-conducting, pure and uniform in quality, and of very low specific gravity (1.15). It may be reduced to an exceedingly fine powder, and is insoluble, does not melt, and decomposes only at high temperatures.

The name Arkosite is derived from the word "Arkose," the district in which the deposit occurs being characterized by outcroppings of arkose sandstone. It can be readily incorporated with organic matter and has a distinctly preservative effect on such mixtures in their completed state, fortifying them against the agencies of decay and corrosion. This effect is illustrated by its use with linseed oil for coatings designed to afford protection to metals, fabric, leather, etc. A simple linseed oil film is readily destroyed by the action of acids, alkalis, gases, etc., and will absorb moisture and become an electrical conductor; but the incorporation of enough Arkosite to form a good spreading paint results in a non-conductive, moisture-proof coating which in the laboratory, when spread on steel, could not be broken down by such severe treatment as prolonged immersion in 50 per cent. solutions of sulfuric, hydrochloric, or nitric acid, solution of strong brine, and further exposure to fumes of sulfuric acid, sulfurous acid, nitric acid, sulfuretted hydrogen, and sometimes two or more of these gases at the same time, and in both dry and moist atmospheres. At the completion of these tests the unprotected portions of the steel were heavily corroded. Practical tests of this paint on several steel structures exposed to the most severe conditions have fully confirmed the preliminary laboratory experiments.

One conspicuous effect of the product is to retard the aging of the oil, causing it to remain very tough and elastic. Cloth and leather coatings, after more than four years of exposure, retain their original softness and pliability.

The special merits of Arkosite as an ingredient in rubber compounds have also been carefully demonstrated by exhaustive laboratory tests and in practical service for a period of several years. Its preservative effect upon the rubber and the resistance to deleterious influences imparted to the compounds result in greatly prolonging the life of such goods.

In an ordinary steam hose tube and cover compound, with arkosite filler, the life of the hose is increased 100 per cent.

Similar results are obtained in all classes of rubber goods, depending to a large degree upon the proportion of arkosite (varying from 5 per cent. to 50 per cent.) which can be successfully incorporated in the batch.

The results of the use of arkosite in rubber goods and paints have been outlined here in the hope that they will assist in the solution of problems arising in other lines of manufacture—problems whose final working out may be facilitated or perhaps perfected by the use of such a product.

S. P. THACHER

METALLIC PIGMENTS

Metallic pigments have long been used for purely decorative purposes especially on inside work, but recently aluminum bronze powder is being used for outside work, especially on signs and also on exposed piping, machinery and also buildings where it appears to possess great durability even with a poor vehicle like soluble cotton.

Such pigments as powdered aluminum and zinc or magnesium, metals strongly electro-negative, might be expected to be valuable in protecting iron by electrolytic action and with this idea in mind, paints made of commercial zinc dust with linseed oil and also with Chinese wood oil were tried on strips of sheet steel along with numerous well-known pigments. The test plates were exposed to the weather two years and then for one year inside in a vessel of water. The result of the test was in general in agreement with most other paint tests on iron: that is, that those pigments which have the strongest oxidizing action on the oil are the best—such as red lead, Prussian blue, mixtures of Prussian blue and chrome yellow and basic lead chromate. Also it appeared that some pigments which usually give poor results on iron, such as carbon black, yet when used with a small amount of oil give good results. It appears that for an iron-protecting paint the hygroscopic nature of a pure linseed oil film should be destroyed either by using a pigment which alters its character by oxidation or by using a large amount of a finely divided inert pigment to "close up the pores of the oil." As for the zinc dust paint, neither of these results would be expected, yet its condition was better than any of the rest at the termination of the test. The coat was perfectly sound without a crack or blister both with linseed and Chinese wood oil. However, whether this good result was due to electrolytic action of the zinc on the iron or to the formation of a firm, coherent film which prevented access of water is not clear.¹

The zinc dust settles out of the vehicle quickly, a fault with a metallic pigment due to its coarseness; in fact, the difficulty of finely powdering a metal is the obstacle to its use.

In addition to any specific chemical action metallic pigments may have either on the vehicle or on the surface painted, they have the important property of opacity, in this respect being far superior to all other light colored pigments, all of which are composed of small particles of transparent substances, the opacity of the paint film being due to refraction and partial reflection from a multitude of superimposed surfaces. Not only is opacity of importance in itself, but there is little doubt that an opaque pigment makes a more durable paint by preventing the destructive action of light on the vehicle. The usually greater durability of dark pigments over light ones may be due to their greater opacity.

Moreover, aluminum and magnesium have a low specific gravity giving large volume and a small tendency to settle.

¹ Whether there is any electrolytic action between the pigment and the iron could be determined by the following experiment. Before the last coat is dry, stick a small piece of foil of the same metal that is used as pigment on the surface of the paint. It would stick there when the paint dried and from time to time could be brought into electrical connection through a sensitive galvanometer with the iron plate. If the pigment is more electronegative than the iron, as is zinc or aluminum, a potential higher in the iron than in the piece of metal foil would show electrolytic action, varying no doubt with the amount of moisture absorbed by the paint film from the surrounding medium.

Now that cheaper methods of powdering metals have been developed, metallic pigments are more available for use, and the fact that such pigments are of a wholly different character chemically and physically from all others would make systematic tests of such pigments both for wood and iron of great interest; the desirability of such tests is respectfully suggested to those having paint tests in charge.

D. DAVIDSON

478 SHERIDAN AVE.
DETROIT, MICH.

SURFACE COMBUSTION

Editor of the Journal of Industrial and Engineering Chemistry:

The Gas and Oil Combustion Company of New York City, appreciating the tremendous value of the so-called Surface Combustion or Flameless Fires, has succeeded in combining all the inventors and inventions in this field, such as Lucke, Bone, McCourt, Schnabel, Ellis and various other interests. We are in absolute control to-day of all these inventions, past and present, and of any which may be made by these various gentlemen in the future. This action has been taken since we recognize that in order to achieve success in the development of this field, it is advisable to have all the interests represented by the various inventors combined, thereby avoiding friction and litigation, as well as creating coöperation.

HUGO LIEBER

ANNUAL TABLES OF CONSTANTS: PHYSICAL, CHEMICAL AND TECHNOLOGICAL, VOLUME II

The second volume of the Annual Tables of Constants, Physical, Chemical and Technological, published by the International Commission appointed by the VIIth International Congress of Applied Chemistry, will be sold to subscribers at \$6.00 (unbound), provided the subscription is sent in before Jan. 31, 1913.

Members of the American Chemical Society are entitled to a 20 per cent. reduction (making a net price of \$4.80 for the unbound edition), provided the subscription is sent in before Jan. 31, 1913.

Subscriptions should be sent either to the University of Chicago Press, Chicago, Ill., or to Dr. Charles Marie, Secretary, 9 Rue de Bagneux, Paris, France.

THE DETERMINATION OF CHROMIUM AND VANADIUM IN STEEL—A CORRECTION

In my article under the above title, *THIS JOURNAL*, 4, 589, the titration of the vanadium in the excess of permanganate must be done with sodium arsenite, not with ferrous sulfate. Ferrous sulfate reduces the vanadic acid simultaneously with the permanganate and gives an indefinite end point.

D. J. DEMOREST

A NEW FORM OF ORSAT APPARATUS—A NOTE

Editor of the Journal of Industrial and Engineering Chemistry:

I note in *THIS JOURNAL*, 4, 898, in the article under the above title, that Mr. L. M. Dennis calls attention to an absorption pipette, making up part of the apparatus adopted by the Chemists' Committee of the Steel Corporation for the analysis of gases, and states that while copyrighted it is quite similar to the form proposed by Hankus twelve years earlier. The Babb Modification of the Orsat Apparatus, containing this form of pipette, has been advertised and sold by Messrs. Eimer & Amend for quite a number of years, and in this region has always been considered the creation of Mr. J. H. Babb; so common is this knowledge that we did not deem it necessary to make this simple acknowledgment in our pamphlet. In adopting and making this excellent device a part of the apparatus we use, it was without any pretense or purpose of claiming originality.

J. M. CAMP

BOOK REVIEWS

Transactions of the American Institute of Chemical Engineers.

Volume IV (1911). Office of the Secretary, Polytechnic Institute, Brooklyn, New York. Published by the Institute through D. Van Nostrand Company, New York, 1912. 8vo., iv + 514 pages.

This fourth volume presents, as a frontispiece, an excellent brown tone photograph of the Institute's President, Leo H. Baekeland. The volume is larger than any of its predecessors and indicates the conservative but steady growth of this infant among chemical societies. The binding is the garnet buckram familiar among Van Nostrand publications. It is safe to predict, however, that the binding is not well enough done for such a heavy volume and that it will, therefore, not stand much usage. The contents of the volume are divided into two main divisions: Institute Proceedings and Reports (pp. 1-86) and Addresses and Papers read before the Institute (pp. 87-505).

The editor of the volume, Dr. John C. Olsen, who is also the Secretary of the Institute, is to be congratulated upon the successful production of a well arranged and pleasing volume and especially one with so few errors as appear from a rapid perusal of the volume. It might not be out of place to suggest, however, that a different arrangement of the table of contents would at least save some from making the error of thinking all of the table of contents is on page iii.

Among the miscellaneous material in the first eighty-six pages is an account of the 3rd semi-annual meeting (Chicago), the two most notable features of which were the series of visits to factories and the first award of the Institute medal to Mr. F. J. Wood, of Marx and Rawolle, Brooklyn, New York, for his

work on multiple effect distillation of glycerine. The series of factory visits at this meeting were easily the finest series of such visits it has ever been the pleasure of the writer to attend. There is also an account of the fourth Annual Meeting (Washington, D. C.), the most important feature of which was the Symposium on the United States Patent System. This division of the volume contains also a copy of the Institute's Constitution and a list of the membership.

The main body of the volume contains the following addresses and papers read before the Institute:

- Some Problems in Chemical Engineering Practice.
- Extraction of Bismuth from Carbonaceous Ores.
- Classen Lignum Company.
- Plant of the Kentucky Soda Ash Company.
- Introduction to Washington Address.
- Manufacture of Chloroform from Bleaching Powder and Ethyl Alcohol.
- Construction of Laboratory Apparatus.
- Manufacture and Testing of Shipping Cylinders for Anhydrous Ammonia.
- F. W. Frenichs.
- Manufacture and Testing of Carbonic Acid Cylinders, John C. Minor, Jr.
- Report of the Committee on Chemical Engineering Education, Samuel P. Sadtler.
- Circular Letter No. 2, Committee on Chemical Engineering Education.
- The Four-Year Course in Chemical Engineering, Jos. H. James.
- The Question of Five-Year Engineering Courses at Ohio State University, Jas. R. Withrow.
- A Course in Chemical Engineering Education, J. C. Olsen.
- Industrial Chemical Calculations, Jos. W. Richards.
- The Practical Value of Determination of British Thermal Units on Anthracite Coal, S. F. Peckham.
- Two Methods of Testing Asphalt, S. F. Peckham.
- Explosives Used in Engineering and Mining Operations, Clarence Hall.
- Problems in the Manufacture of C. P. Acids, J. T. Baker.

Combustion of Pulverized Coal, L. S. Hughes.

Distribution of Power in Portland Cement Manufacture, Richard K. Meade.

Hardening of Plasters and Cements and a Simple Chronographic Apparatus for Recording Set, Chas. F. McKenna.

The Manufacture of Gelatine, Ludwig A. Thiele.

The Adaptation of the Centrifugal Pump to Chemical Problems, F. G. Wheeler.

Symposium on the United States Patent System, Papers read at Washington Meeting, The United States Patent Office, E. B. Moore.

Protection of Inventions by Patents: Existing Defects and Remedies, Walter D. Edmonds.

The United States Patent System, Robt. N. Kenyon.

Report of Committee on Patents, Wm. M. Grosvenor.

This array of papers shows clearly that the Institute has maintained its high position of the year before in the number and character of papers read before it as well as in the broad field of chemical industry and engineering covered. A prominent feature of the year's work is the continued interest in the problems of Chemical Engineering Education as is shown by the group of four papers along this general line. One of these papers is the Report of the Institute Committee on this topic. The Institute's work in stirring up interest along this line alone (impossible in any other chemical organization) will always be a justification for the Institute.

Another and perhaps more important feature of the year's work on the part of the Institute was the thorough handling of the situation regarding the conditions existing in the present United States Patent System. This again is a subject which could be taken care of only by an organization such as the Institute, where about every member has personal experience in the practical difficulties encountered under the present patent system. Many in our own greatest Chemical Society have long felt the need of just such work, but have utterly failed to accomplish anything in a society which very properly is least interested in manufacturing. The Institute is to be congratulated upon the position it has assumed in this matter and upon being able to present a symposium containing such papers as the one by United States Commissioner of Patents, Moore, the progressive program for existing evils of Mr. Edmonds, the paper by Mr. Kenyon of the New York bar and the Institute Committee Report by its Chairman, Dr. Grosvenor. Leaders of the Washington bar were also present and entered into the discussion; their opinions are instructive if not always believed.

Prominently noticeable also is the series of papers or addresses by retiring President F. W. Frerichs. That some of these are quite old disclosures is true, but they are nevertheless disclosures and hence of value in showing how certain actual difficulties were met and overcome. May we have many more of such! Largely in this same category also is the paper on problems in the manufacture of C. P. acids by Mr. J. T. Baker. Our thanks go out to him for taking the time from a busy life to give us these insights. If the things were familiar to some of us, we must also have had the feeling that Mr. Baker had done more than most of us in educating those about us and we cannot but hope that the good example set will bear even better fruit than contributed discussions.

Time or space do not permit more extended comment, but it would be an oversight indeed if we did not mention the thorough address on the adaptation of the centrifugal pump to chemical problems by F. G. Wheeler. This article is well illustrated and comes from one of extended and constant factory contact and who, therefore, speaks with authority. The volume will be interesting to a wider field than merely to chemical engineers and industrial chemists.

JAMES R. WITHROW

The World's Cane Sugar Industry, Past and Present. By H. C. PRINSEN GEERLIGS, late Director of the Sugar Experiment Station, Pekalongan, Java. Quarto, xvi + 399 pp. Illustrations, Plates, Maps and Diagrams. Printed and published by Norman Rodger, Altrincham, England, 1912. Price, 12 s.

The accomplished author of the above volume having previously given the world a view of the technical side of raw cane sugar production in his two books entitled "Cane Sugar and its Manufacture" and "Chemical Control in Cane Sugar Factories," now turns to the broader consideration of the subject and presents a historical review of the industry.

This work presents a most comprehensive discussion of the influences, geographical, climatological, political and commercial which have affected the development of the cane sugar industry. Having been an eyewitness of its decline and then its revival, the author has felt the more impelled to chronicle the steps in the changes and development of so important an industry. The most important of these he considers to be the Brussels Convention, the Conquest of Formosa by the Japanese, the tariff privileges granted by the United States to the former Spanish Colonies and last, but not least, the great advance of science in the province of cane sugar manufacture—all of which has occurred during the last twenty years.

The first part of the work treats of the general history of the cane sugar industry, beginning with the legendary origin of the sugar cane along the banks of the Ganges, and its development in tropical countries from earliest times until the latter part of the eighteenth century, when European wars did so much to disturb and injure it.

Then it was that sugar from the beet began to interest scientists, economists, governments. Napoleon lent his powerful aid to the establishment of this industry, which struggled through obstacles of ignorance, opposition and misrepresentation. The French government protected the raw beet sugar by duties upon French colonial sugars and increased surtaxes on foreign sugars. The abolition of slavery in the West Indies in the first half of the nineteenth century also seriously impaired the cane sugar industry. The author considers at considerable length and most interestingly the various excise regulations of the principal European governments relating to the production, exportation, importation and consumption of sugars, and the influences which all of these had upon the cane sugar industry, particularly the incidents leading up to the Brussels Convention in 1902 and the abolition of bounties on exported beet sugars.

In the second part of the book the author describes the condition of the cane sugar industry in the different countries of production with such thoroughness as to constitute it a veritable encyclopaedia of the subject. Here are found recorded the geographical data for each country, carefully compiled statistics in regard to climate, the varieties of cane, their diseases and insect pests, the methods of cultivation and manufacture, customs of the population, commercial practices, cost of production, governmental regulations, statistics of production and everything which the owner, manufacturer or merchant could find of value.

The great mass of detail is well presented and accompanied by good illustrations as well as excellent maps, not only of the individual cane sugar-producing countries showing the cane districts in detail, but also by two novel maps of the world showing graphically the cane sugar production of each country in 1900 and in 1910.

The author has the courage of his convictions too, for he does not hesitate to prophesy the future of the industry in the important countries of production. This feature of the work but emphasizes its great value to all who are in any way financially or commercially interested in the industry.

The various Asiatic countries are first considered in the list of producing countries, then Spain and the several countries of the Americas, followed by the countries of Africa and of Australia.

One wonders at the patience and thoroughness with which this work has been executed, for while the author quotes his

very numerous authorities and states that the work is largely due to personal correspondence with authorities on the subject in well nigh every cane sugar producing country, it is easy to see that the masterly discussion of the entire subject which pervades every part of the work could be given only by one having an extraordinary grasp of the subject and an unusually effective manner of presenting it.

The publisher has done his work admirably in the printing and binding, turning out, with good print on good paper, a volume which will prove an ornament as well as a satisfaction.

In short, the book is one which will be a highly appreciated addition to sugar literature and of inestimable value to those who are interested in the industry.

W. D. HORNE

Hydro-Metallurgy of Copper. By W. E. GREENWALT. Cloth, octavo, pp. 504 + x. Illustrated. McGraw-Hill Book Co., New York. 1912. Price, \$5.00.

For years metallurgists have waited for a new work on the hydro-metallurgy of copper. While many papers on this subject have been written, appearing periodically in the technical journals, text-books have contained but limited descriptions. Probably this is due to the poor results which have been obtained by the numerous processes proposed for the extraction of copper from its ore by wet methods.

On reading Mr. Greenwalt's book we hardly feel, however, that it has covered the ground in an entirely satisfactory manner, though the author has had a great deal of experience in this branch of metallurgical work and has undoubtedly spent a vast amount of time in collecting data on the numerous wet metallurgical processes that have been brought before the public during the past many years. The descriptions of these processes are extracts from the technical journals (to which reference is made) and are given in quite a lengthy manner, but no conclusions are drawn in any individual case as to why they were not successful.

Part I of the work deals with the preparation of ore and roasting, and in the 151 pages devoted to this branch of the subject it would seem that too much space is given to descriptions of roasting operations, which are more or less antique at the present time. The discussion of "objects of roasting" and the various reactions taking place is excellent, even if a little lengthy.

Part I closes with a chapter on typical examples of roasting and in this we find attention paid to the roasting of Cripple Creek ores, which would seem hardly a good example of the work on this subject, and but little information is given in regard to examples of roasting copper ores.

In Part II, after discussing the properties and solubilities of copper, the author takes up the subject of hydro-metallurgical processes in general dividing these processes into two heads: (1) Purely Chemical, and (2) Electrolytic. To these descriptions of the numerous processes 190 pages are devoted. The list covers not only processes which have been tried but various patented ideas which have never been put in actual practice.

In connection with electrolytic processes, the writer states that "Ever since success was achieved in electrolytic refining of blister copper, metallurgists have naturally asked why similar operations could not be successfully applied in the extraction of copper direct from its ores." And shortly after states that "it is quite probable that electrolytic methods of extraction will be in general use in the near future." It is hoped that this prediction may come true. The writer's conclusions in regard to the difficulties encountered in this process, however, are not always correct, as for example his remarks on the subject of insoluble anodes.

After this follow brief chapters giving descriptions of the various methods that have been proposed for treating zinciferous copper ores, copper ore and matte, the precipitation of copper from mine waters, the production of copper sulfate, the apparatus and appliances used in wet methods and power data.

The last chapter is devoted to economic considerations, and in this the writer very correctly states that the siliceous copper ores offer the best opportunity for hydro-metallurgical work. The difficulty of maintaining the electrolyte in the proper condition is, however, only slightly dwelt upon. In spite of its shortcomings, this book will be found most valuable as a reference work for numerous processes we have heard of from time to time and the chemistry and manipulation of which we may desire to look up in connection with new propositions.

ARTHUR L. WALKER

Soil Conditions and Plant Growth. By EDWARD J. RUSSELL. Longmans, Green and Co., London, 1912. pp. 168. Price, \$1.50, net.

In the preface the author states that in this volume he has endeavored to give a concise account of our present knowledge of the soil as a medium of plant life. "As a result of its history the subject is now in a rather confused state." In recent years, however, its recognition as a basis of technical importance, whilst the remarkable constitution it appears to possess, the variety of its microscopic inhabitants and their close connection with plant life, all impart to its study unusual scientific interest. The time, therefore, seems ripe for a critical examination of the foundations for our beliefs, and this task is rendered easier by the advances made of late years on the Continent, in America and in this country."

The book is divided into seven chapters as follows: I. Historical and Introductory, 18 pages. II. The Requirements of Plants, 32 pages. III. The Constitution of the Soil, 27 pages. IV. The Carbon and Nitrogen Cycles in the Soil, 24 pages. V. The Biological Conditions in the Soil, 18 pages. VI. The Soil in Relation to Plant Growth, 12 pages. VII. Soil Analysis and its Interpretation, 17 pages.

In the first chapter, the author has outlined briefly the most important ideas relative to the soil and plant growth which have existed from the middle of the 16th century to the present time. The other six chapters contain brief statements of well established facts and a résumé of the most important recent research along the line of the subjects treated. In addition there is an appendix giving a brief outline of the method of soil analysis and a selected bibliography.

Mr. Russell's wide experience has qualified him especially for this work and he has succeeded admirably in his "endeavor to give a concise statement of our present knowledge of the soil as a medium of plant growth." The book is well written and will prove interesting reading to all interested in agriculture.

F. B. CARPENTER.

Henley's Twentieth Century Book of Recipes, Formulas and Processes. Edited by GARDNER D. HISCOX, M.E. Large 8vo., 787 pp. New York: The Norman W. Henley Publishing Co. Price, \$3.00 net.

The editor has endeavored to meet the requirements of the mechanic, the manufacturer, the artisan, and the housewife. The book is closely written, the principal headings being: Adhesives, Alloys, Beverages, etc., Cleaning Preparations and Methods, Cosmetics, Perfumes, Ceramics and Stone, Dyes, Enameling, Food Adulterants, Household Formulas, Inks, Oils and Paints, Photography, Plating, Polishes, Soaps, Solders, Varnishes and Waterproofing.

In the several thousands of recipes, there has been no effort to use any one standard system of measurement. Several systems often appear on the same page; there are no references, and no index is given.

Although the book is not scientific, it contains a great mass of material which may be of interest to many, but it is not of sufficient technical value to meet the needs of the manufacturer or chemist.

R. K. MURPHY

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York

Analysis, Detection, Determination, and Separation of the Chemical Elements. Vol. I. By A. RUEDISULB. 8vo. Price, \$4.75. M. Drechsels, Berne. (German.)

Boilers, Steam, and Boiler Accessories. By W. INCHLEY. Cr. 8vo., pp. 412. Price, \$2.40. Longmans, Green & Co., New York.

Cast Iron, Influence of Silicon on the Characteristics of. By P. PAGLIANTI. L. 8vo., pp. 18. Price, \$0.50. Dissertation, University Aix-la-Chapelle. (German.)

Cellulose Pulp, The Manufacture of. By E. KIRCHNER. L. 8vo., pp. 264. Price, \$3.00. A. Dorn, Biberach. (German.)

Ceramic Chemistry. By H. H. STEPHENSON. 8vo., pp. 85. Price, \$1.50. Davis Bros., London.

Chemical Industry of the German Empire, 1912, Directory and Articles of Commerce of the. By OTTO WENZEL. 12th edition. 8vo., pp. 1500. Price, \$8.00. Rudolf Mueckenberger, Berlin.

Chemical Technical Calculations. By FERDINAND FISCHER. 8vo. Price, \$0.75. Otto Spamer, Leipzig. (German.)

Concrete, Reinforced. By K. ALLTISCH. L. 8vo., pp. 214. Price, \$1.25. F. Deuticke, Vienna. (German.)

Cotton Waste, Its Production, Manipulation and Uses. By THOMAS THORNEY. 8vo. Price, \$2.00. Scott, Greenwood & Son, London.

Dictionary of Applied Chemistry, Vol. III. Grain Lac—Oils. By EDWARD THORPE. 8vo., pp. 789. Price, \$12.00. Longmans, Green & Co., New York.

Electrochemistry, Practice of. By FRANZ FISCHER. 8vo., pp. 130. Price, \$1.25. Julius Springer, Berlin. (German.)

Encyclopedia of Chemical Science Applied to the Industrial Arts. Vols. I and II. By C. CHABRIE. 12 vols. L. 8vo., pp. 1100. Price, \$9.00. Paris. (French.)

Engines, Gas and Oil. (Translation.) By A. KIRSCHKE. 8vo., pp. 160. Price, \$1.00. Scott, Greenwood & Co., London.

Essential Oils: Semi-Annual Report of Schimmel & Co., Oct., 1912. Sm. 8vo. Fritzsche Bros., New York.

Explosives, Modern, Historical Papers on. By GEORGE W. MACDONALD. 8vo. Price, \$2.00. Whittaker & Co., London.

Explosives, "Miedziankit," a Substitute for Dynamite. ANON. 8vo., pp. 46. Price, \$0.50. Gebroeder Boehm, Kattowitz. (German.)

Fuel Values, Comparative, of Gasoline and Denatured Alcohol in Internal-Combustion Engines. By R. M. STRONG AND LAUSON STONE. 8vo., pp. 243. U. S. Bureau of Mines, Bulletin 43.

Glass Manufacture. By ROBERT DRALLE. L. 8vo., pp. 1269. Price, \$11.00. R. Oldenbourg, Munich. (German.)

Hygiene, The Science of. By WALTER C. C. PAKES AND A. T. NANKIVELL. Sm. 8vo., pp. 164. Price, \$1.75. D. Van Nostrand Co., New York.

Inorganic Analysis, Theoretical and Practical Principles of. By G. CHESNEAU. 8vo., pp. 642. Price, \$5.00. Ch. Beranger, Paris. (French.)

Lampblack and Printers' Ink, The Manufacture of, from Refuse and By-products. By HIPPOLYT KOEHLER. 3rd edition. L. 8vo., pp. 228. Price, \$2.00. F. Vieweg & Sohn, Braunschweig. (German.)

Legal Chemistry. By R. DE FORCRAND. 8vo., pp. 387. Price, \$2.00. H. Dunod & E. Pinat, Paris. (French.)

Lubrication and Lubricants. By L. ARCHBUTT AND R. M. DEELEY. 3rd edition. Roy. 8vo., pp. 636. Price, \$6.50. London, 1912.

Mining, The Physics and Chemistry of. By T. H. BYROM. Sm. 8vo., pp. 188. Price, \$1.00. Crosby, Lockwood & Son, London.

Motors, Explosion-proof, An Investigation of. By H. H. CLARK. 8vo., pp. 44. U. S. Bureau of Mines, Bulletin 46.

Nitrogen, Utilization of Atmospheric. By THOMAS H. NORTON. 8vo., pp. 178. Bureau of Manufactures, Dept. of Commerce and Labor, Report No. 52.

Organic Chemistry, The Theories of. By FERDINAND HENRICH. 8vo., pp. 402. Price, \$2.75. F. Vieweg & Sohn, Braunschweig. (German.)

Organic Compounds, The Preparation of. By E. DE BARRY BARNETT. 8vo. Price, \$2.25. J. & A. Churchill, London.

Petroleum and Its Products, Methods for the Determination of Water in. By IRVING C. ALLEN AND WALTER A. JACOBS. 8vo., pp. 13. U. S. Bureau of Mines, Technical Paper 25.

Petroleum, Identification and Knowledge of the Hydrocarbons of. By J. TAUSZ. 8vo., pp. 75. Price, \$0.50. Dissertation, Polytechnic Institute, Karlsruhe. (German.)

Retort Settings, Modern: Their Construction and Working. By T. BROOKE. 8vo., pp. 212. Price, \$2.00. John Allan & Co., London.

Rubber. By RUDOLF DITMAR. 8vo., pp. 140. Price, \$1.75. Julius Springer, Berlin. (German.)

Sugar: The World's Cane Sugar Industry, Past and Present. By H. C. PRINSEN-GEERLIGS. L. 8vo., pp. 369. Price, \$3.00. Norman Rodger, Manchester.

Testing Materials, The Art of. By F. W. HINRICHSSEN. Lex. 8vo. Price, \$4.50. Ferdinand Enke, Stuttgart. (German.)

Vinegar Making from Waste Grapes. 8vo. California Agricultural Experiment Station, Bulletin 227.

RECENT JOURNAL ARTICLES

Bleaching Cotton. By J. MERRITT MATTHEWS. *Textile World Record*, Vol. 44, 1912, No. 2, pp. 216-220.

Boiler Plants, The Use of Coal in, Steam. By T. F. J. MAGUIRE. *Steam*, Vol. 10, 1912, No. 6, pp. 153-159.

Brewing, Origin and History of Beer and—from Prehistoric Times to the Beginning of Brewing Science and Technology. By JOHN P. ARNOLD. 8vo. Institute of Fermentology, Chicago.

Carbon Monoxid, Determination of Small Quantities of. By O. BRUNCK. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 48, pp. 2479-2481.

Cellulose, Formylated. By EDWARD C. WORDEN. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 22, pp. 1064-1068.

Cements, Portland, The Constitution of. By CECIL H. DESCH. *Chemical World*, Vol. I, 1912, No. 12, pp. 405-407.

Coal, The Carbonization of. By VIVIAN B. LEWES. 8vo., pp. 311. Price, \$1.75. John Allan & Co., London.

Coal, The Storage of. By EVERARD BROWN. *Steam*, Vol. 10, 1912, No. 6, pp. 162-164.

Coking by Destructive Distillation, Advances in. By F. SCHREIBER. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 45, pp. 2289-2296.

Dyes, Azo-salicylic Acid and Azo-hydroxynaphtholic Acid. By ANUKUL CHANDRA SIRCAR AND EDWIN ROY WATSON. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 20, pp. 968-971.

Electrolysis, The Theory of Ions and. By A. HOLLARD. 8vo., pp. 220. Price, \$1.00. Gauthier-Villars, Paris. (French.)

Explosions of Methyl Alcohol Vapors, The Danger of. By K. ARNDT. *Chemiker Zeitung*, Vol. 36, 1912, No. 138, pp. 1350-1352.

Furnace, The Electric, for Brass Melting. By G. H. CLAMER AND CARL HERING. *American Institute of Metals*, Advance Copy, 1912, pp. 16.

Gas Illuminating, The Legal Specifications for. By E. B. ROSA AND R. S. MCBRIDE. *American Gas Light Journal*, Vol. 97, 1912, No. 22, pp. 342-343 and 346-350.

Hydrogen, Newer Methods for the Production of. By A. SANDER. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 47, pp. 2401-2407.

Hypochlorite Production, Sodium, Some Factors in the Coat of. By W. H. WALKER AND R. F. GEGENHEIMER. *Chemical Trade Journal*, Vol. 51, 1912, No. 1330, pp. 513-514.

Iron Charcoal, The Effect of High Carbon on the Quality of. By J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 10, 1912, No. 12, pp. 777-788.

Lead in Lead Colors, Determination of. By A. UTZ. *Farben-Zeitung*, Vol. 18, 1912, No. 1, pp. 18-20.

Linseed Oil and Turpentine, Density and Thermal Expansion of. By H. W. BEARCE. *Paint and Varnish Record*, Vol. 6, 1912, Nos. 3 and 4, pp. 30-32 and 26-32.

Oils and Fats in Leather, Determination of. By CHARLES R. OBERFELL. *Journal of the American Leather Chemists' Association*, Vol. 7, 1912, No. 12, pp. 656-664.

Oils, Fatty, The Hexabromid Numbers of, and the Determination of Rape Seed Oil in Crude Linseed Oils. By A. EIBNER AND H. MUGGENTHALER. *Farben-Zeitung*, Vol. 18, 1912, Nos. 3 and 4, pp. 131-134 and 175-177.

Oils, Lubricating, Viscosity of. By A. E. DUNSTAN AND J. F. STEVENS. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 22, pp. 1063-1064.

Ozone, Apparatus for Working with, and for its Quantitative Determination. By HUGO BRACH. *Chemiker-Zeitung*, Vol. 36, 1912, No. 136, pp. 1325-1327.

Painting by Dipping and Spraying. By A. S. JENNINGS. *Oil and Colour Trades Journal*, Vol. 42, 1912, No. 736, pp. 1416-1419.

Rubber, The Desulfurization of Vulcanized. By PAUL ALEXANDER. *Chemiker-Zeitung*, Vol. 36, 1912, No. 133, pp. 1289-1291.

Silk, The Weighting of, with Tin Phosphate. By HERMANN LEY. *Chemiker-Zeitung*, Vol. 36, 1912, No. 145, pp. 1405-1407.

Sugars in Leather, Determination of. By F. P. VEITCH AND J. S. ROGERS. *Journal of the American Leather Chemists' Association*, Vol. 7, 1912, No. 12, pp. 645-656.

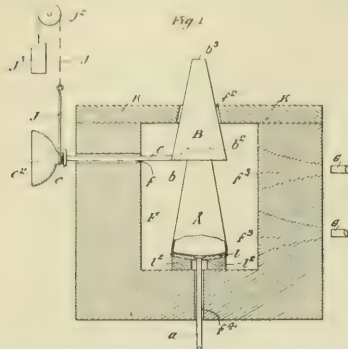
Textile Chemistry. The Use of Organic Preparations as Solvents and as Temporarily Active Adjuncts in. By FRANZ ERBAN. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 46, pp. 2343-2348.

Weighing in Analytical Work. By RICHARD KEMPF. *Chemiker-Zeitung*, Vol. 36, 1912, No. 138, pp. 1349-1350.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

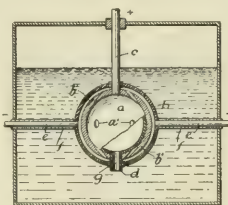
Alkali-Metal Cyanids. J. A. Kendall, Aug. 27, 1912. U. S. Pat. 1,037,010. In this process nitrogen and an alkali metal compound are heated to a high temperature in the presence of carbon. In using the apparatus illustrated, the nitrogen and alkali metal compound, such as fused sodium carbonate, pass downward



through pipes D and E respectively into reaction chamber A, which is filled with carbon. Heat is supplied by the surrounding furnace and the cyanid produced is condensed in the condenser B from which it is withdrawn through pipe c. The non-volatile matter or ash may be removed from time to time through pipe a.

Attaching Rubber to Metals. Leo Daft, Aug. 27, 1912. U. S. Pat. 1,036,576. The metal to which the rubber is to be attached is first electroplated, using an electrolytic bath made from an alloy containing copper and zinc and an alloy containing copper, zinc and antimony and the rubber is attached to the plated surface by vulcanization.

Oxidizing or Reducing Chemical Substances by Electrolysis. Geo. Kolsky, Sept. 24, 1912. U. S. Pat. 1,039,415. This apparatus is intended primarily for the electrolytic production of hypochlorates, chlorates, perchlorates, and persulfates, the patentee having found that the reactions for the production of these compounds may be facilitated by placing either the cathode within the anode or the anode within the cathode. In the apparatus the anode is in the form of a hollow sphere, a, having a number of lateral perforations a', similar to what is known as the "Witt Stirrer." The sphere a is surrounded by a second hollow sphere, b, forming the cathode. The outer sphere is also perforated, the perforations having the form of oblong openings. The anode is mounted upon a shaft, c, which passes through the cathode and by means of which it is rotated to circulate the electrolyte into contact with the anode and cathode.



Removing Carbon from Cylinders, Valves and Rings of Gasoline Engines. C. Elliott and C. Kelly, Sept. 10, 1912. U. S. Pat. 1,038,324. This method consists in placing a fusible metal or alloy in the engine cylinder and melting this metal or alloy by the heat generated in the cylinder.

Hydrogenated Butter Substitute. C. Ellis, Sept. 17, 1912. U. S. Pat. 1,038,545. This is a butter-like composition consisting of

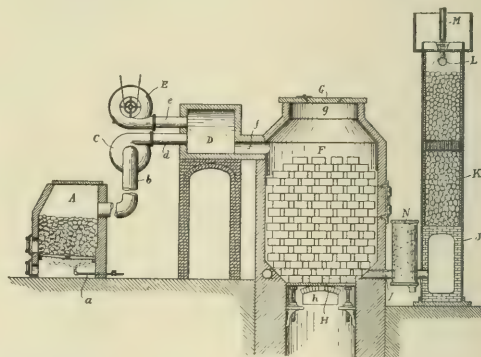
an emulsion of a hydrogenated vegetable oil and milk, from which emulsion the excess of moisture has been expressed.

Process of Hydrogenation. C. Ellis, Oct. 8, 1912. U. S. Patent 1,040,531. In this process oily material comprising unsaturated bodies is heated and moved in a traveling stream through a plurality of beds of porous solid material comprising a catalytic body. A countercurrent of a hydrogen-containing gas is simultaneously passed through the porous beds. The excess hydrogen is removed and again becomes a part of the counter gaseous current. The oil is removed and at least a portion of it becomes a part of the traveling stream of oil.

Alcohol. K. Keifer, Oct. 15, 1912. U. S. Pat. 1,041,298. The patentee prevents the development of bacteria and detrimental ferments as well as the so-called after-taste in alcoholic drinks by impregnating the sweet wort with carbonic acid gas under pressure, and fermenting the wort under pressure, using as a yeast a ferment accustomed to a large amount of carbonic acid.

Treating Feldspar to Recover Potassium Salts. Morse and Sargent, Oct. 15, 1912. U. S. Pat. 1,041,327. In this process, feldspar at an elevated temperature is subjected first to the action of a sulfate of calcium and secondly, to that of an alkali chlorid or an alkaline earth chlorid whereby there are produced oxids of sulfur, a soluble compound of potassium and a residual material capable of being converted easily into Portland cement. It is stated that it is the production of the oxids of sulfur and the cement material in connection with that of the soluble potassium compound that makes possible the economical production of the latter.

Sodic-Silico Aluminate and Hydrochloric Acid. A. H. Cowles, Oct. 15, 1912. U. S. Pat. 1,041,598. In this process naturally occurring materials containing silica and alumina, such as clay, bauxite, feldspar and the like, are mixed with sodium or potas-



sium chlorid, and carbonaceous matter. The mixture is formed into briquets and placed in a down-draft furnace of the character shown in the accompanying illustration. Steam, air and fuel gases, from oil, gas or powdered coal are admitted from above and the waste gases together with water vapor and hydrochloric acid gas are drawn off from the bottom.

Alcohol from Sulfite Liquor. Gösta Ekström, Oct. 22, 1912. U. S. Pat. 1,042,332. Sulfite liquor from the sulfite pulp process contains saccharine matters which by fermentation may be converted into ethyl alcohol. Before such fermentation

can be successfully carried out it is necessary to remove the sulfurous acid present. When this acid is neutralized by means of quicklime, limestone or the like, a number of organic acids, notably lactic acid, are formed which react with the organic compounds present in which the sulfurous acid is loosely bound, transferring the sulfurous acid into compounds injurious to the yeast.

The patentee adds to the sulfite liquor ammonium sulfate which reacts with the unstable organic compounds, its negative ions combining with the lime of such compounds while the sulfurous acids of such compounds are set free. The sulfite liquor is then neutralized with quicklime, limestone or the like and liquor fermented.

Available Phosphoric Acid. J. H. Connor, Oct. 29, 1912. U. S. Pat. 1,042,400. In this process phosphatic rock or other naturally occurring phosphatic material is reduced to a size to pass through a screen of sixty meshes to the inch. Soda ash, crushed limestone and iron oxid are mixed with it and the mixture heated to from 2000 to 3000 degrees F., until the phosphoric acid becomes soluble.

Nitrogen Compounds. Pettibone and von Sholly, Oct. 22, 1912. U. S. Pat. 1,042,141. This process is designed to provide an economical method of manufacturing cyanamid and other nitrogen compounds, and at the same time to utilize a by-product in the nature of spent gas, after the heat units have been utilized for the production of heat or power. In the practice of the process, fire is kindled in the generator and a good producer gas generated from liquid or solid fuel and delivered by the centrifugal extractor and fan G into holder H. In the operation of the exhaust fan G air will be drawn through the heating chamber E into the generator, and hot gas will be drawn from the generator through the tubes of the heater, thereby heating the air circulated around the tubes. The gas is also

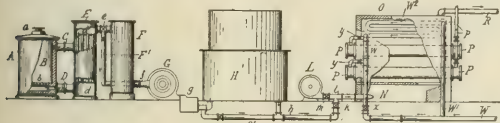


FIG. 1

drawn through the scrubber F where it is freed from ash and cinder. A store of gas being accumulated, it is admitted to the burner N, together with a regulated air supply, and ignited, the proportions of gas and air being regulated to produce perfect combustion without material excess of either gas or air in the chamber around the retorts P. The resulting products of combustion are substantially free of both air and unburnt gas. A jet exhauster will draw the products of combustion from the combustion chamber of furnace O and deliver them

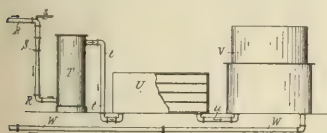
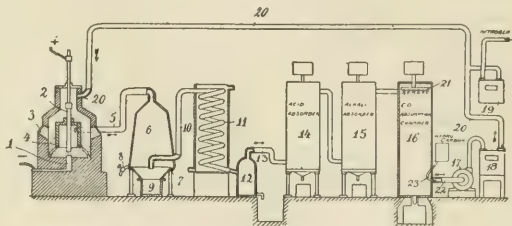


FIG. 2

purified gas, consisting of nitrogen, 99.3 per cent., and other gases, seven-tenths of one per cent., is stored in the holder V, from which it is supplied to the retorts as required. The retorts being heated to a red heat, approximately 800° C., are charged with carbids and halogen salts, mixed in suitable proportions, introduced at the rear ends, and the lids tightly closed. The carbids and halogen salts being heated to the proper temperature, the valves *y* are opened, admitting nitrogen which has been preheated

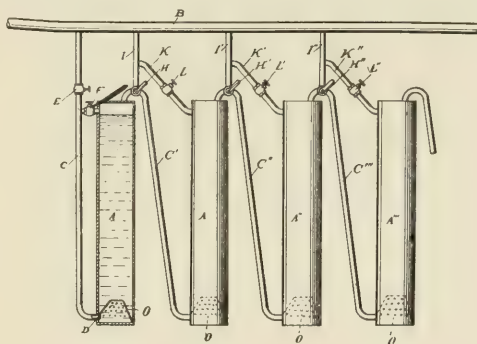
in the coil W², and which passing in contact with the red hot charge causes a chemical reaction to take place between it and the carbid mixture which is expressed by the following equation, using calcium carbide as an example: $\text{CaC}_2 + \text{N}_2 = \text{CaNCN} + \text{C}$. The result of the reaction is a complete conversion of the carbide into cyanamids and carbon. The conversion being completed, the nitrogen is shut off, the charge drawn from the retorts, cooled in an atmosphere of cool nitrogen gas, and a fresh charge of carbide mixture introduced and the process repeated.

Making Nitrogen Compounds Including Nitride and Ammonia. Sinding-Larsen, Oct. 29, 1912. U. S. Pat. 1,042,723. In this process minerals containing metals or metalloids which can be directly transformed into nitrogen compounds are vaporized in an atmosphere which contains nitrogen and a reducing agent



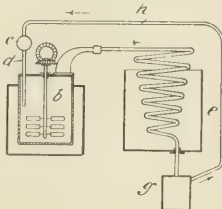
such as a hydrocarbon in a state of gas or vapor. The products obtained are led away, separated and collected. Among the minerals mentioned as being suitable for use in the process are feldspar, kaolin, apatite, limestone and dolomite. The accompanying illustration shows apparatus in which the process may be carried out.

Pitch from Coal-Tar, Petroleum Residues, Creosote, Schist Oils, etc. Henri Hennebutte, Nov. 12, 1912. U. S. Pat. 1,044,175. In this process the coal tar or like material to be converted into pitch is first mixed with a solvent such as tar, the boiling point



of which is higher than that of the hydrocarbons under treatment. The mixture is then heated and a current of air driven slowly through it. The oxygen of this air is nearly all absorbed by the mixture, causing a transformation of it into pitch.

Formic Acid. J. Weise, Nov. 12, 1912. U. S. Pat. 1,043,985. This process is designed to increase the yield of formic acid in preparing it from the reaction



both closed off against the access of outer air.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF DECEMBER, 1912

ORGANIC CHEMICALS

Acetanilid.....	Lb.	20 1/2 @	23
Acetic Acid (28 per cent.).....	C.	2.00 @	2.15
Acetone (drums).....	Lb.	16 1/2 @	17 1/2
Alcohol, grain (188 proof).....	Gal.	2.55 @	2.57
Alcohol, wood (95 per cent.).....	Gal.	50 @	52
Alcohol, denatured (180 proof).....	Gal.	40 @	42
Amyl Acetate.....	C.	2.65 @	2.85
Aniline Oil.....	Lb.	10 1/8 @	10 5/8
Benzoic Acid.....	Lb.	23 @	27
Carbon Tetrachloride (drums).....	Lb.	9 1/4 @	9 3/4
Carbon Bisulfide.....	Lb.	8 1/2 @	9
Chloroform.....	Lb.	25 @	35
Carbolic Acid (drums).....	Lb.	14 @	15
Citric Acid (domestic), crystals.....	Lb.	38 1/2 @	39
Camphor (refined in bulk).....	Lb.	44 @	—
Dextrine (imported potato).....	Lb.	6 @	7
Dextrine (corn).....	C.	2.75 @	3.06
Ether (U. S. P., 1900).....	Lb.	14 @	20
Formaldehyde.....	Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....	Lb.	18 1/2 @	19
Oxalic Acid.....	Lb.	7 1/8 @	8 1/8
Pyrogalllic Acid (bulk).....	Lb.	1.35 @	1.45
Salicylic Acid.....	Lb.	31 @	33
Starch (corn).....	C.	2.00 @	2.11
Starch (potato).....	Lb.	5 1/4 @	5 3/4
Tannic Acid (commercial).....	Lb.	35 @	35 1/2
Tartaric Acid crystals.....	Lb.	30 1/4 @	31

INORGANIC CHEMICALS

Acetate of Lime (gray).....	C.	2.50 @	2.60
Acetate of Lead (brown, broken).....	Lb.	7 3/4 @	8
Alum (lump).....	C.	1.75 @	2.00
Aluminum Sulfate.....	C.	90 @	1.75
Ammonium Carbonate, domestic.....	Lb.	8 @	8 1/2
Ammonium Chloride, gray.....	Lb.	6.15 @	6 1/4
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4 @	2 1/2
Arsenic, white.....	Lb.	5 1/8 @	5 3/8
Brimstone (crude, domestic).....	Ton	22.00 @	22.50
Barium Chloride.....	C.	1.35 @	1.40
Barium Nitrate.....	Lb.	5 @	5 1/4
Borax, crystals (bags).....	Lb.	3 3/4 @	4 1/4
Boric Acid, crystals (powd.).....	Lb.	7 @	7 1/2
Bromine, bulk.....	Lb.	25 @	30
Bleaching Powder (35 per cent.).....	C.	1.40 @	1.60
Barytes (prime white, foreign).....	Ton	18.50 @	22.50
Blue Vitriol.....	Lb.	5 1/2 @	5 3/4
Calcium Chloride.....	C.	65 @	90
Chalk (light precipitated).....	Lb.	4 @	5
China Clay (imported).....	Ton	11.50 @	18.00
Feldspar.....	Ton	7.00 @	9.00
Fuller's Earth, powdered.....	C.	80 @	85
Green Vitriol (bulk).....	C.	55 @	60
Hydrochloric Acid (18°).....	C.	1.15 @	1.55
Iodine (resublimed).....	Lb.	3.05 @	3.10
Lead Nitrate.....	Lb.	8 1/8 @	8 1/4
Lithium Carbonate.....	Lb.	65 @	70
Magnesite (raw).....	Ton	7.50 @	8.50
Nitric Acid, 36°.....	Lb.	3 7/8 @	4 1/4
Phosphorus.....	Lb.	35 @	90
Phosphoric Acid, sp. gr. 1.75.....	Lb.	21 1/2 @	25 1/2
Plaster of Paris.....	Bbl.	1.50 @	1.70
Potassium Bromide.....	Lb.	35 @	37
Potassium Permanganate (bulk).....	Lb.	9 3/4 @	10
Potassium Cyanide (bulk) 98-99%.....	Lb.	19 @	24
Potassium Iodide (bulk).....	Lb.	2.60 @	2.65
Potassium Chlorate, crystals.....	Lb.	8 1/4 @	9 1/2
Potassium Nitrate (crude).....	Lb.	5 @	—
Potassium Bichromate, 50°.....	Lb.	6 1/4 @	7

Quicksilver, Flask.....		40.00 @	—
Salt Cake (glass-makers').....	C.	55 @	65
Silver Nitrate.....	Oz.	40 1/4 @	42
Soapstone in bags.....	Ton	10.00 @	12.00
Sodium Acetate.....	Lb.	4 1/4 @	5
Sodium Chlorate.....	Lb.	8 1/4 @	9 1/2
Sodium Bicarbonate (English).....	Lb.	2 3/4 @	3
Sodium Bichromate.....	Lb.	5 @	5 1/8
Sodium Hydroxide, 60 per cent.....	C.	1.60 @	1.65
Sodium Hyposulfite.....	C.	1.30 @	1.60
Sodium Nitrate, 95 per cent., spot.....	C.	2.60 @	—
Sodium Silicate (liquid).....	C.	65 @	1.50
Strontium Nitrate.....	Lb.	6 7/8 @	7 1/8
Sulfur, Roll.....	C.	1.85 @	2.15
Sulfur, Flowers (sublimed).....	C.	2.20 @	2.60
Sulfuric Acid, 60° B.....	C.	85 @	1.00
Talc (American).....	Ton	15.00 @	20.00
Terra Alba (American), No. 1.....	C.	75 @	80
Tin Bichloride (50°).....	Lb.	14 1/4 @	14 1/2
Tin Oxide.....	Lb.	52 @	54
Zinc Chloride (granulated).....	Lb.	4 1/4 @	4 1/2
Zinc Sulfate.....	Lb.	2 1/4 @	2 1/2

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	42 @	45
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2 @	14
Castor Oil (No. 3).....	Lb.	9 1/2 @	10 1/2
Ceresin (yellow).....	Lb.	12 @	22
Corn Oil.....	C.	5.80 @	5.85
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	39 @	40
Cylinder Oil (light, filtered).....	Gal.	21 1/2 @	32
Japan Wax.....	Lb.	9 3/4 @	10
Lard Oil (prime winter).....	Gal.	94 @	98
Linseed Oil (double-boiled).....	Gal.	44 @	—
Paraffine Oil (high viscosity).....	Gal.	26 @	28
Paraffine (crude 120 & 122 m. p.).....	Lb.	3 1/4 @	3 3/4
Rosin Oil (first run).....	Gal.	36 @	37
Spindle Oil, No. 1.....	Gal.	18 @	19
Sperm Oil (bleached winter), 38°.....	Gal.	72 @	74
Stearic Acid (double-pressed).....	Lb.	9 1/2 @	10 1/4
Tallow (acidless).....	Gal.	65 @	68
Tar Oil (distilled).....	Gal.	30 @	31

METALS

Aluminum (No. 1 ingots).....	Lb.	26 @	26 1/2
Antimony (Hallet's).....	Lb.	9 1/2 @	10 1/4
Bismuth (New York).....	Lb.	2.10 @	2.15
Copper (electrolytic).....	Lb.	17.40 @	17.60
Copper (lake).....	Lb.	17 1/2 @	17 5/8
Lead, N. Y.....	Lb.	4.30 @	—
Nickel.....	Lb.	50 @	55
Platinum (refined).....	Oz.	46.00 @	—
Silver.....	Oz.	63 1/4 @	—
Tin.....	Lb.	49.90 @	—
Zinc.....	Lb.	7.30 @	—

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	3.22 1/2 @	3.25
Fish Scrap, domestic, dried.....	Unit	nominal	—
Blood, dried.....	Unit	2.70 @	2.75
Tankage, high grade.....	Unit	2.65 @	10
Bone, 4 1/2 and 50, ground, raw.....	Ton	28.50 @	—
Potassium, "muriate," basis 80%.....	Ton	38.55 @	—
Phosphate, acid, 16 per cent.....	Ton	6.75 @	7.00
Phosphate rock; f. o. b. mine:			
Florida land pebble, 68 per cent.....	Ton	3.70 @	3.80
Tennessee, 68-72 per cent.....	Ton	4.25 @	4.50
Pyrites, furnace size, imported.....	Unit	0.13 1/4 @	0.13 1/2
Castor meal.....	Unit	nominal	—
Mowrah meal.....	Ton	9.00 @	—

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

FEBRUARY, 1913

No. 2

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhenny, Wm. McMurtrie, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Contributions and communications should be addressed to the Editor, M. C. Whitaker, Columbia University, New York City

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

Cooperation among Chemists and Manufacturers . . . 92

The Present State of the Art of Industrial Management . . . 93

ORIGINAL PAPERS:

The Hydrogenation of Oils. By Carleton Ellis 95

Boron: Its Properties and Preparation. By E. Weintraub 106

Acetylene Solvents. By Joseph H. James 115

Tests on the Opacity and Hiding Power of Pigments. By G. W. Thompson 120

An Application of the Electric Resistance Furnace to the Determination of Oxygen in Iron and Steel. By R. H. McMillen 123

The Volumetric Determination of Manganese in Rock; Slags, Ores and Spiegels. By F. J. Metzger and L. E. Marrs 125

Antiseptic Tests of Wood Preserving Oils. By A. L. Dean and C. R. Downs 126

The Oxygen Absorption Test for Linseed Oil. By Hans Mannhardt 129

A Rapid and Accurate Gravimetric Method for Determining Milk-Fat in Evaporated Milk and Milk Powders. By E. P. Harding and Guy Parkin 131

The Rate of the Reaction of Nitrous Acid and Urea in Dilute Solutions. By W. D. Bonner and E. S. Bishop 134

The Influence of a Preceding Crop on Nitrification in Soil. By T. Lyttleton Lyon and James A. Bizzell 136

A Comparison of Some Qualitative and Quantitative Methods for Carbonates in Soils. By E. W. Gaither 138

A Contribution to Our Methods of Determining Nitrogen in Humus. By Charles B. Lipman and H. F. Pressey 143

LABORATORY AND PLANT:

The Manufacture and Properties of Sublimed White Lead. By John A. Schaeffer 144

A New Form of Laboratory Extraction Apparatus. By A. E. Perkins 148

A Device for Controlling Small Electric Furnaces. By Charles Burton Thwing 149

Gas Bubble and Washing Tube for Combustion Apparatus. By H. E. Smith 150

A Modified Extraction Apparatus. By G. M. MacNider 150

A Reflux Condenser. By S. W. Wiley 151

ADDRESSES:

Tar Distillation in the United States—General Development and Recent Progress. By R. P. Perry 151

Disposal of Sewage with Recovery of Elements of Plant Food for Use in Agriculture. By William McMurtrie 156

Manufacture and Uses of Cyanamid. By E. J. Pranke 159

CURRENT INDUSTRIAL NEWS:

United States Statistics for 1912 161

The Chemical Activities of Belgium 161

The Increased Use of Charcoal Iron 161

Gilled Tubing 161

The Toxicity of White Lead 161

Tantalum as a Substitute for Platinum 162

Sulfur in Illuminating Gas 162

The Use of Gases for Fire Extinction on Board Ship 162

A New Timber Preserving Process 163

The Billiter Alkali-Chlorine Cells 163

Water Purification in the Industries 163

The Slate-Bed Treatment of Sewage 163

The Manufacture of Swedish Filter Paper 164

The Minimization of Fire Risks in the Case of Inflammable Liquids 164

The British Starch Industry 165

The Sulfite Waste Liquor Problem 166

"Sacchulose" 166

NOTES AND CORRESPONDENCE:

A Standard Viscosimeter and Standard Methods for Determining Viscosities—Why not? 167

The Use of a Light Filter Cell in Polarizing High Grade Sugars 167

The Analysis of Unsweetened Evaporated Milk 168

The Determination of "Volatile" in Coal 169

New Chief of Bureau of Chemistry 170

Electrolytic Copper Refining in Norway 171

Growing Use of Ammonium Sulfate in China 171

American Chemical Society Spring Meeting 171

"The Progressive Age" becomes "The Gas Age" 171

Obituary—Alfred Bellamy Aubert 171

BOOK REVIEWS:

A Handbook of Sugar Analysis; Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines; Textbook of Chemical Technology and Metallurgy; Die Synthese des Kautschuks; Soil Fertility and Fertilizers; Das Hydrosulfid; The Analysis of Paint and Varnish Products 172

NEW PUBLICATIONS 175

RECENT INVENTIONS 176

MARKET REPORT 178

EDITORIALS

COOPERATION AMONG CHEMISTS AND MANUFACTURERS

Men in a calling which has so many ramifications as has chemistry in its various applications to all modern activities, must cooperate if the profession, as a whole, is to advance symmetrically and uniformly.

Before such cooperation can be effective, mutual understanding between the profession and the manufacturer must be achieved. It is true that many of the chemical manufacturers still follow the old rule of thumb methods without themselves having any notion of the underlying principles which are unchangeable and inexorable. These manufacturers must be brought to see the actual existence of such principles and to realize that an understanding, as well as strict compliance therewith, is necessary for the attaining of that measure of success which is necessary in order to maintain uniform quality and maximum output of finished product.

The organizers of the Eighth International Congress of Applied Chemistry, which recently met in New York, endeavored to bring about some such mutual understanding between the manufacturers on the one hand, and the educators and those who practice chemistry as a profession on the other. To this end more than two hundred chambers of commerce and eight thousand manufacturers in the United States, as well as over two hundred and fifty educational institutions were appealed to in special bulletin setting forth the points in which cooperation between these three representative divisions would be valuable and helpful. The commercial side, as represented by the chambers of commerce and manufacturers, was informed, in effect, that our educational institutions felt that the complaints, so frequently made by those engaged in commercial pursuits, of the lack of intellectual equipment possessed by young chemical graduates, were due in a large measure to the policy of secretiveness followed by our chemical manufacturers. They were appealed to to break down this policy of secrecy and to cooperate with our educational institutions, so that the record of The Eighth International Congress, as reported in its proceedings, would disclose to our foreign visitors a hearty cooperation between the educational and manufacturing institutions of our country. On the other hand, the duty of cooperation with the manufacturer was urged upon the educational institutions.

The results have shown that neither the manufacturers nor the educators responded to the suggestions of the organizers of the Congress. This is to be regretted, for it is not likely that such another opportunity will be offered in this country for fifty years or more. However, the seed has been sown; the idea and its need still exist. Let us all work together to the end that it may not be very many years before such cooperation will become an accomplished fact.

The American Chemical Society, with its membership of more than six thousand, represents to-day the

greatest, the strongest, the most active, and the most virile association of chemists in the world. It is through the members of the American Chemical Society, associated as they are in forty or more sectional units, that such cooperation seems most likely to be finally accomplished.

In New York City, the chemist who is to be appointed to the Municipal Board on Combustibles and Explosives is selected by the Mayor from among three names submitted to him for that purpose by the New York Section of the American Chemical Society. Efforts are now being made to obtain similar cooperation in other departments of the City of New York government. Chemists have cooperated in the purchasing bureau of the city, and in less than three years the savings effected by them run into tens of thousands of dollars annually.

Similar efforts at municipal cooperation are likewise successful in Boston and Philadelphia. These facts brought to your attention now may act as a seed-crystal around which your own efforts may crystallize.

The efforts made by those in charge of the Eighth International Congress of Applied Chemistry, and the New York Section of the American Chemical Society, show that making converts to the cause of cordial cooperation is a slow and laborious proceeding, particularly in chemistry, because, while the work of the chemist is fundamental and essential, that fundamental and essential character is not always obvious to the lay mind. That is the reason why, in making converts, you will meet with very meager and slow results at the start. While it may take you years to get the Government and the manufacturers to work with the chemist, the value of the result should spur you on to greater effort rather than cause you to lose heart.

Probably the broadest opportunity to raise the standard of the chemical profession in the United States, to bring about better understanding between manufacturers on the one hand and the chemists on the other, to promote acquaintance, personal, social, and otherwise among those who practice chemical pursuits, is in an institution like the Chemists' Club of New York City. While this club is located in New York City, it is not alone for the chemists of New York, but it is devoted to the interests of the chemical profession of the entire United States. It knows no state, no sectional boundary. Its field ranges over the entire domain of chemistry; those with whom it seeks to cooperate and those whom it seeks to benefit, are those of us who teach, practice, or apply chemistry anywhere in the United States. The Chemists' Club is organized on the broadest lines conceivable.

You ask what the Chemists' Club can do for those in the south and west. A chemist residing at a distance greater than twenty-five miles from the Building in New York City, and not regularly doing business in the city, is entitled to non-resident membership for \$10.00 per year. Now what do non-resident mem-

bers get for that \$10.00? The Chemists' Club has its home in the Chemists' Building, which is the only building in the world erected for the particular and peculiar benefit of the chemical profession. It has laboratories from the top floor down to the sixth; it has two floors of sleeping rooms; it has a good restaurant and a good social room; it has a good library. A non-resident member coming to New York can put up at the Chemists' Club as he would at a hotel, and if he finds that he needs a laboratory for a week or ten days or a month or six months, he can have it. The Club has three laboratories for rent to transients.

You may come to New York to sell a product or a process, and it may be necessary to make a laboratory demonstration. You cannot walk into somebody's else laboratory, and get the necessary accommodation and the necessary privacy. You may be a man without a country and a stranger without a home, but you need not be either if you are a non-resident member of the Chemists' Club. You may live, have every laboratory facility and enjoy the use of a most valuable chemical library in this building in the center of the city. You cannot do that in any other city in the world. No technical organization in any country offers so much to its non-resident members as does the Chemists' Club in New York City.

Many of you have been in a position where you have wanted a certain volume of the *Berichte*, the *Annalen*, or any one of a number of other journals or a textbook, or have wanted a translation into English of some French, German, or Italian reference. Non-resident members of the Club telegraph or write to the Club librarian and receive that particular volume by return mail; if the book is not in duplicate, transcripts will be made of the portions that you want and will be mailed to you; at the end of the month you will get your bill for services which will be made at cost since the Club is not run for profit.

Some of you may not need literature, but it is just possible that you may want some chemical that is not stocked by any of the chemical dealers in the United States. If the plans of those in charge of the Chemists' Club do not miscarry it will be only a short time when by telegraphing or writing to the Chemists' Club they will be able to take out of their museum an original package of the chemical that you want but cannot buy in the United States, and mail it to you; you in turn will order from the maker, at your convenience, an exact duplicate of the original package to replace the one loaned you by the Chemists' Club. What have you gained? You have saved the expense of a cable, consequent delay, and a fuss at the customs house. The American chemist, next to membership in the American Chemical Society, has never been offered a better opportunity for coöperation than membership in the Chemists' Club.

The development of the Club Library is an example of coöperation. Mr. Herman Frasch has most generously donated \$10,000, the income from which is to go for the purchase of new books. Prof. Chas. F. Chandler, of New York City, has donated practically all of his private library, and Prof. John W. Mallett,

of the University of Virginia, donated practically all of his library; the American Chemical Society and the New York Section of the Society of Chemical Industry have given their books; we also have the benefit of the Sir William Henry Perkin Library Fund, and the Charles Frederick Chandler Library Fund. Numerous members have donated parts or all of their working libraries, and the libraries of several of our deceased members have passed into the possession of the Club. The aim of the Chemists' Club is to get together the most complete set of books on chemical subjects in existence, and further to have as many as possible of them in duplicate, so that we may have a circulating library of immense proportions.

Those of you who are members of the Chemists' Club, or the American Chemical Society, or both, will find that the best and the most useful resting place for such of the books in your library for which you yourself have no further use, will be in the custody of the Chemists' Club.

The Chemists' Club further maintains an employment bureau for the use of chemists, whether members or not, who are out of a position; this bureau does not seek to aid those already in a position to better themselves; all it does is to give a man a start, and once he has that he must make or break himself. By notifying the employment bureau of the Chemists' Club of vacancies in your district or by sending to it names and addresses of worthy chemists who are out of positions, you will be adding greatly to the effectiveness of that bureau which has for many years past helped hundreds of men annually in obtaining good positions and in enabling many manufacturers to get suitable chemical assistance with little delay.

We have pointed out only a few of the opportunities for coöperation, and dilated upon the benefits that the Chemists' Club will confer upon the individual chemist and upon the chemical profession as a whole. The field of coöperation is too big to do more than merely to scratch the surface and commend it to your serious consideration and to solicit your earnest support.

B. C. HESSE

THE PRESENT STATE OF THE ART OF INDUSTRIAL MANAGEMENT

The American Society of Mechanical Engineers have made, through a sub-committee of that organization, a most careful study and an elaborate report on the present status of the efficiency movement in industrial work. They have carefully analyzed the problem and classified their conclusions in by far the most important contribution so far submitted on this subject. We have carefully summarized their work in the following abstract:

During the past few years a number of striking phenomena, in connection with industrial management, must have become evident even to the most superficial observer. The more important are:

(a) The wide-spread, popular interest in the subject which had its rise in a statement made before the Interstate Commerce Commission, in a hearing on the matter of proposed advances in freight rates, that by

the application of newly discovered principles of management "in the railroad operation of this country an economy of \$1,000,000 a day is possible." This popular interest is shown by the great number of articles published in the daily papers and popular magazines, mediums that give but scant attention to technical subjects except of the most striking nature.

(b) The suddenly intensified interest in the subject on the part of employers and business executives in many lines of activity, shown by lectures, addresses, professional papers and reports presented to their associations.

(c) The opposition of labor unions to the newer methods of management, shown by statements of labor leaders, in a few instances by strikes, and by an attempt to prohibit by law the use of some of these methods in Government shops.

(d) Government recognition of the matter shown by the appointment of a special committee of the House to investigate systems of management in Government arsenals and shops, which reported in March, 1912; by the appointment of a civilian board by the Secretary of the Navy to investigate management in the navy yards, which reported in July, 1911; and by a Senate bill, S 6172, now in committee, which is intended to prohibit time study and the payment of premiums or bonus on Government work.

(e) The rapidity with which literature on the subject has accumulated. One directory of books on business management lists 500 titles, and states that 75 per cent. of them have been written within five years.

(f) The formation of two societies having as an aim the furtherance of the applications of the principles of management.

(g) The separation of persons interested in the matter into two camps, one of enthusiastic advocates, the other of vigorous opponents of what is called the new element in management.

(h) The unquestionable proof of the advance that can be made in unskilled work, as shoveling material, and in ancient trades, as bricklaying, by the application of the principles of management. This is the most striking phenomenon of all.

Before defining the element in the art of management that has given rise to these phenomena, it is necessary to review briefly the beginnings of modern industry. This gives a historical setting from which the present can be more truly judged.

Modern industry was brought about by the change from handicraft to manufacture, and early British economists held that the application of the principle of *division of labor* was the basis of manufacture.

It appears, however, that another principle is the basic one in the rise of industry. It is the *transference of skill*. The transference of skill from the inventor or designer to the power-driven mechanism brought about the industrial revolution from handicraft to manufacture.

No better single illustration of the application of this principle can be found than in the invention of the lathe slide rest by Henry Maudsley, in 1794. So

complete has been this transference of skill that today hand tooling is a vanished art in American machine shops. Very few lathe hands can chase a thread with hand tools, yet all can cut good threads on an engine lathe, thanks to the slide rest.

Methods of analyzing and recording operations were early developed. Adam Smith recorded the divisions of the work of manufacturing pins, listing all operations. Charles Babbage gave a table from a French investigator showing the number of operations, time for each, cost of each, and expense of tools and material for making pins in France in 1760.

Thus we see the application of the principle of *transference of skill* at the basis of the development of the industry, and an early application of the value of the detailed study of operations in making that transference more complete. But the machine was the viewpoint. It was looked upon as the producing unit. The subsequent development has had the effect of advancing still further the division of labor, and beginning the division of thought. The drafting room presents the first example of this trend, in its collection of engineering data, in its prediction of results and the formation of staff organization. The art of machine design has been greatly developed. The last half of the last century saw a tremendous increase in inventions, a tremendous furtherance of the application of transference of skill to machine and tools. The skeleton of an industrial organization of this period, one that was too large for a single executive to manage, consisted of a designing department and a production department, each with a head responsible to the manager.

The first of these, the one that was the means of embodying skill in the machinery and tools of production, was highly developed and organized. Experiment, research and detailed study were constantly resorted to, to aid in reaching the desired result. The work was highly specialized and the employees highly paid. Not infrequently the manager or chief executive devoted much of his own time to this part of the business.

The production department presented a contrasting condition. The workmen were given the tools and machines designed in the drawing-room and using their own unaided skill were expected to produce work of the desired quality and quantity. Except in rare instances, no effort was made to transfer the skill of the management to the production department and to the employees, or to undertake the division of executive thought. Very little consideration was given to the workmen as a producing unit.

Within the past 20 or 25 years certain changes have taken place in the attitude of many production managers toward the problems that they face and the forces and means that they control. An early evidence was the development of profit-sharing, premium and bonus systems to reward increased effort and output. There followed welfare work, industrial betterment movements, the adoption of safeguards and regulations to minimize industrial accidents, the substitution of the principle of accident compensation for

employers' liability and an improvement in the physical surroundings and conditions of factories. All of these tendencies have been fostered and to a great extent initiated by employers. But even today these are by no means generally adopted.

Another tendency, less pronounced in character, has as its object the improvement of the personal relations between the employees themselves and between the employee and the employer. It is the effort to establish the best of factory working conditions in those things not physical in nature, to develop and maintain a shop atmosphere free from all harassing and hindering influences. It is an attempt to make use of the results of experimental psychology in improving working conditions.

But the most important change and one that comprehends the others, is in the mental attitude toward the problems of production. The tendency is toward an attitude of questioning, of research, of careful investigation of everything affecting the problems in hand, of seeking for exact knowledge and then shaping action on the discovered facts. It has developed the use of time study and motion study as instruments for investigation, and the planning department as an agency to put into practice the conclusions drawn from the results of research, and methods of wage payment which stimulate coöperation.

All of these changes have affected the production department much more than the designing department. The effect is to extend the principle of trans-

ference of skill to production, so that it completely embraces every activity in manufacture. The skill of management is consciously transferred to all of the operations of the factory. This extension is expressed by these phases; the drawing-room is the planning department of design, and the planning department is the drawing-room of production.

To obtain information on present conditions, the committee wrote to the recognized experts, to executives of plants in many lines of industry, to students of industrial problems, and it has had many interviews with men in these various fields. The responses to the requests were in the main most generous, and the replies convey the ideas of a conscious effort to ascertain and study facts and systematically to apply them to instructing the workmen and in controlling every department of industry. Setting these against the underlying principle of the transference of skill, they conceive the prominent element in present-day industrial management to be: *the mental attitude that consciously applies the transference of skill to all the activities of industry.*

Here emphasis is placed upon the word *all*, for the restricted application of this principle to machines and tools has been highly developed for a long period. But its conscious application in a broad way to the production departments, and particularly to the workmen, we believe has been made during the last quarter century.

ORIGINAL PAPERS

THE HYDROGENATION OF OILS¹

By CARLETON ELLIS

The treatment of unsaturated oily bodies with hydrogen to obtain saturated derivatives is of great scientific and technical interest. In the fat industry a most fascinating problem has been that of the conversion of oleic acid or olein into stearic acid or the corresponding glyceride.

Oleic acid and hydrogen combine, molecule for molecule, to yield stearic acid according to the reaction:



Thus 282 pounds of oleic acid require 2 pounds (or about 0.7 per cent.) of hydrogen for the production of 284 pounds of stearic acid, and similarly the transformation of olein into stearine requires the use of about 0.68 per cent. hydrogen.

One thousand cubic feet of hydrogen weigh approximately 5.6 pounds, hence a pound of olein calls for a little over 0.1 of an ounce of hydrogen equivalent to approximately 2500 cubic feet of hydrogen per ton (of 2000 pounds) of olein. Thus by weight only a relatively small quantity of hydrogen is needed, while by volume the amount required, of course, is considerable.

Many attempts to hydrogenate oleic acid have been

made. Reviewing this subject in 1897¹ Lewkowitsch refers to the ease with which the lower members of the oleic series are converted into saturated acids and states that "oleic acid itself resists all attempts at hydrogenization," further remarking that he had "carried out a large number of experiments in this direction under most varied conditions, but hitherto all of these gave negative results."

Prior to this, however, Goldschmidt, in 1875,² had reduced oleic acid by means of hydriodic acid and amorphous phosphorus at 200-210° C. This presumably led to the attempted commercial development of a process by de Wilde and Reyckler³ involving heating oleic acid to 280° C. with 1 per cent. of iodine, adding and melting therein a certain quantity of tallow soap, and then boiling with acidulated water. The product was then distilled and the iodine, in part, recovered from the pitch. The yield of stearic acid or saturated fat is stated to be approximately 70 per cent. of the theoretical. Only about two-thirds of the iodine could be recovered so the process apparently did not find technical use.⁴ Should the much lauded method of treating kelp, primarily for obtaining potash salts, come into use, a cheap supply of iodine

¹ J. S. C. I., 389 (1897).

² Sitz. b. d. Wiener Akad. d. Wiss., 72, 366.

³ Bull. Soc. Chim., [3] 1, 295 (1898).

⁴ Chem. Ztg., 1889, 595.

¹ Presented before the New York Section of the Society of Chemical Industry, November 22, 1912.

would be available which might then make the Wilde and Reychler process of some technical interest.

Chlorine in lieu of iodine has been tried, but great difficulty has been experienced in securing an autoclave of resistant material. Imbert¹ recommends using quantities of chlorine and alkali exactly calculated on the iodine number of the fatty acid and operating at a temperature of 120° to 150° C. and pressure of about five atmospheres for a period of six hours.

Zürer² chlorinates the fatty acid and then heats with water in the presence of a finely divided metal as zinc or iron. Lewkowitsch alleges that the treatment of monochlor-stearic acid in this manner causes a reversion to oleic acid.

Tissier, in 1897,³ lays claim to a process for the reduction of oleic acid by nascent hydrogen. Powdered metallic zinc is placed in an autoclave, water and the fatty material containing olein introduced and treated under pressure.

Under the circumstances the glyceride is hydrolyzed to fatty acid and glycerine, and according to Tissier nascent hydrogen is evolved by virtue of the finely divided metal and reduces the oleic to stearic acid. Freundlich and Rosauer⁴ claim the Tissier process to be inoperative.

The conversion of oleic acid into palmitic and acetic acids by means of caustic potash in accordance with the Varentrapp reaction⁵ has not proved to be of much commercial significance, although it appears that certain firms have been making use of the process in a limited way.

The Schmidt zinc chloride process⁶ involves heating oleic acid and zinc chloride at exactly 185° C. while interaction is taking place. "Deviation from this point leads to an increase of liquid substance. Unfortunately the solid candle material must be distilled and the considerable proportion of β -hydroxystearic acid (melting point 82° C.) in the crude product is seriously diminished by the partial conversion of this acid into oleic and iso-oleic acids. Thus, from a candle-maker's point of view, a substance of high melting point is rendered practically valueless. Schmidt's process was tried on the large scale in an Austrian candle works. The quantity of liquid *unsaponifiable* substance obtained was, however, so large that commercial success was out of the question."

Many processes have been proposed based on the well-known action of sulfuric acid on oleic acid. Hydroxy-stearic acid is obtained by steaming the product. It would lead us too far from the present subject to enter into any further discussion of these reactions.

PROCESSES INVOLVING APPLICATION OF ELECTRICITY

In 1886, Weineck⁷ called attention to the possibility of electrolytic addition of hydrogen to oleic

acid. Kuess¹ later attempted to apply the electric current in the steam distillation of fatty acids.

In patents taken out by Magnier, Bragnier and Tissier,² the fatty material is acidified with sulfuric acid, whereupon the acidified mass is mixed with 5 to 6 times its weight of water and then under a pressure of 5 atmospheres is subjected to the action of an electric current, which generates hydrogen in a nascent state.

An interesting method of converting oleic into stearic acid is that comprised in the Hemptinne electric discharge process. The method is carried out by interposing a thin layer of the oil in the path of an electric discharge, while bringing hydrogen into contact with the oil.³

Fig. 1 shows the arrangement of apparatus for this purpose. The conversion is effected in a chamber having an inlet pipe, H, furnishing hydrogen under constant pressure. Oleic acid is supplied by a pipe, O, to a sprinkling device which discharges the acid onto a system of parallel plates consisting of the glass

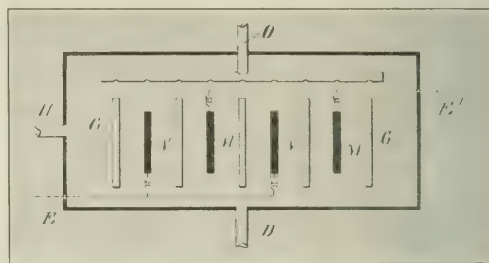


FIG. 1

plates G and alternately the metal plates M, N. The metal plates M are connected to one pole, the others, N, being connected with the other pole of a source of electricity. As the oil passes over the plates the electrical discharge causes conversion of some oleic acid into stearic acid, and analogous compounds having melting points in the neighborhood of 69° C.

Hemptinne prefers to work at pressures less than atmospheric. The yield is lower at atmospheric pressure. By treatment in this manner it is not difficult to secure a yield of 20 per cent. of stearic acid. Repeated treatment permits even up to about 40 per cent. yield. Here, as so often elsewhere, the effect of mass action becomes manifest and as the content of stearic acid increases the speed of reaction greatly decreases. Much better results are obtained by saturating to the extent of about 20 per cent., removing the stearic acid by pressing, when the oil of reduced stearic acid content is again subjected to the electric discharge, and a further 20 per cent. yield obtained. The oleic residue contains liquid condensation products amounting to about 40 per cent. of the total weight. It is stated that the presence of these bodies

¹ U. S. Patent No. 901,905, of Oct. 20, 1908; see also *Bull. Soc. Chim.*, 1899, 695, 707.

² German Patent No. 62,407, of Aug. 8, 1891.

³ French Patent No. 263,158, of Jan. 16, 1897.

⁴ *Chem. Ztg.*, 1900, 566.

⁵ *J. S. C. I.*, 98 (1883), 200 (1884).

⁶ Lewkowitsch, "Oils, Fats and Waxes," p. 664.

⁷ *Osterr. Privil.*, 10, 400 (July 19, 1886).

¹ *Chem. Ztg.*, 1896, 618.

² Eng. Patent No. 3,363, 1900; German Patent No. 126,446, of Oct. 3, 1899, and additional German Patent No. 132,223.

³ U. S. Patent No. 797,112, of Aug. 15, 1905.

does not impair the market value of what some one has termed "electrocuted" oleic acid.

"J. Petersen¹ also endeavored to reduce oleic acid to stearic acid by allowing an electric current to act between nickel electrodes on an alcoholic oleic acid solution, slightly acidulated with sulfuric acid or preferably with hydrochloric acid. But the yield of stearic acid was small, even under the most favorable conditions, and did not exceed 15 to 20 per cent."

Petersen also endeavored to reduce sodium oleate in aqueous or alcoholic solution to the stearate. No satisfactory results were obtained.

C. F. Böhringer and Sohne² obtained by the same method much better results when using as cathodes, metallic electrodes, which were covered with a spongy layer of the same metal. They recommend as cathodes platinized platinum, and also palladium electrodes covered with a spongy layer of palladium-black. Nickel electrodes are not as effective.

Kolbe³ in 1871 states that Saytzeff reduced nitrobenzol to aniline by passing the vapors of the former, mixed with hydrogen, over palladium-black.

About twenty-five years later Sabatier and Senderens began their classic study of nickel and other metallic catalyzers.

The work of Sabatier and Senderens laid the foundation for the present processes of hydrogenation of oils. Their work is so well known that it is needless to discuss it here.

Fig. 2 shows apparatus used by these investigators in the hydrogenation of bodies capable of vaporization. In this apparatus, 1 is a hydrogen generator; 2 and 3 are wash bottles and 4 is a vaporizer containing

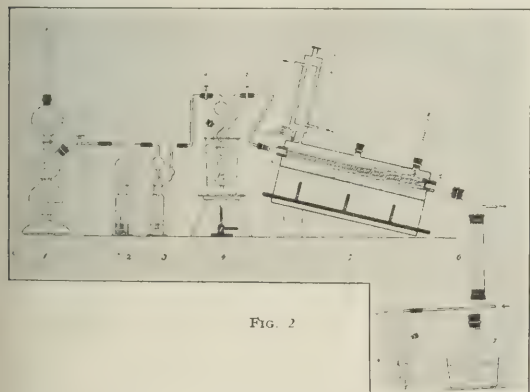


FIG. 2

the substance to be converted into a vapor. 5 is a hydrogenation chamber containing nickel catalyzer and heated by an oil bath. 6 is a condenser.

While a good deal of work has been done on the hydrogenation of fatty oils, the literature on the subject is very meagre indeed and only through the patents which have been issued can we gather from any published records much that is enlightening as to developments in this industry. The patents concerned with

the matter have, moreover, been subjected to a great deal of scrutiny because of the alleged basic character of certain of them. For these reasons the following discussion pertains very largely to processes which have been covered by patents in this country or abroad.

(NOTE.—The illustrations herein are largely derived from the drawings of patent records or have been prepared from written descriptions. All details deemed unnecessary in the portrayal of the essential features of these processes have been omitted. The original records should, of course, be consulted for details.—AUTHOR.)

A German Patent, No. 139,457, of July 26, 1901, to J. B. Senderens, is probably the first patent record having to do with the reduction of organic bodies by hydrogen in the presence of nickel catalyzers. This patent is for the production of aniline from nitrobenzol and involves passing the latter body in the form of a vapor over heated nickel, copper, cobalt, iron, or palladium in the presence of hydrogen. The hydrogen may be in the pure state or in the form of water-gas.

The first disclosure of the possibility of hydrogenation of oils in a liquid state apparently comes from Le Prince and Siveke.¹ In England a corresponding patent (No. 1515, of 1903) was issued to Normann² and the latter patent has become widely known because of its alleged fundamental character.

Normann states that he may carry out the hydrogenation of oils by treatment either in the form of vapors or as liquids. In the former case the fatty acid vapors together with hydrogen may be caused to pass over catalytic material carried by a pumice stone support. This may be represented by Fig. 3

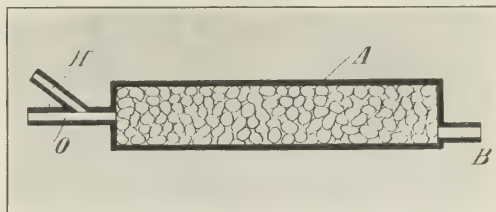


FIG. 3

in which A is a bed containing granular pumice coated with a metal catalyzer. O is an inlet for oil vapors and H is an inlet for hydrogen. The mixture passes through the tube A and the converted material is withdrawn at B. Normann notes, however, that it is sufficient to expose the fat or fatty acid in a liquid condition to the action of hydrogen and the catalytic substance. He states, for instance, if fine nickel powder obtained by the reduction of nickel oxide in a current of hydrogen is added to oleic acid, the latter heated over an oil bath and a strong current

¹ German Patent No. 141,029, of Aug. 14, 1902, Herforder Maschinen- und Oel Fabrik.

² This English Patent is owned by a large soap manufacturing house in England and it is reported they allege the patent in that country to be fundamental and controlling for the hydrogenation of fatty oils generally. They are offering rewards for information as to the secret and unauthorized use of the process and it is said already to have started litigation.

¹ Z. Elektrochemie, 1905, 549.

² Ger. Patents Nos. 187,788, 189,332, 1906.

³ J. prakt. Chem., [2] 4, 418 (1871).

of hydrogen caused to pass through it for a considerable time, that the oleic acid may be completely converted into stearic acid.

Fig. 4 shows very simple apparatus, such as might have been used by Normann to this end. A is a vessel containing oil, O, in which fine particles of nickel are

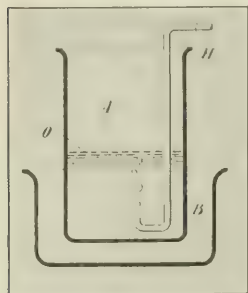


FIG. 4

suspended while a strong current of hydrogen from the pipe H affords the hydrogen requisite for reduction of the oil. By this means Normann treated the fatty acid of tallow having an iodine number of 35 and melting at about 46, thereby converting it into a body of improved color having an iodine number of about

10 and a melting point of about 58. Normann also states that commercial gas mixtures, such as water-gas, may be used in lieu of pure hydrogen.

The disclosures of the Normann patent are, however, rather meagre and hardly can be considered to comprehensively traverse the difficulties encountered in the practical hydrogenation of oils in a liquid state. Dr. David T. Day, of Washington, has brought out a process¹ in which he treats, not fatty oils, but hydrocarbon oils, with hydrogen in the presence of what he terms a porous absorptive substance, mentioning palladium-black, platinum sponge, zinc dust, fuller's earth and other clays. Fig. 5 shows one method proposed by Day to this end.

The upper chamber A is filled with hydrocarbon oil, and porous absorptive material such as palladium-black is introduced in the intermediate chamber C

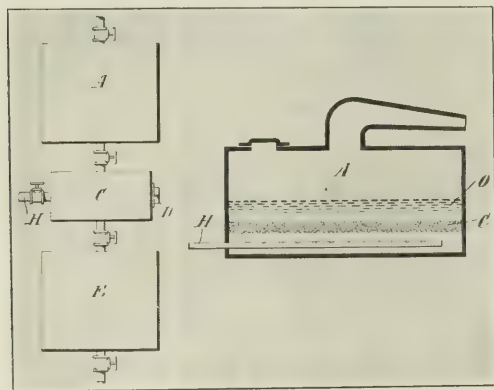


FIG. 5

FIG. 6

by way of the plugged orifice D. Any air present in C may be expelled by flushing out with hydrogen or an indifferent gas. Hydrogen is then admitted by the pipe H until the porous material has absorbed

its full quota. The hydrogen gas may be admitted under a pressure of 100 pounds or more to the square inch. When the porous material in C has become properly charged with hydrogen, the oil is allowed to run from the chamber A through the chamber C into the collecting chamber E, hydrogen being introduced as required by the pipe H.

In the place of hydrogen, Day states that ethylene or other hydrogen carrying gas or vapor may be employed. By this treatment the disagreeable odor of hydrocarbon oil is in great part removed and the burning qualities of the oil improved. When palladium black is used it is recommended that a proportion of one-half ounce to the gallon of oil be taken.

Fig. 6 shows a modification of Day's process. A is an oil still, in the lower part of which the perforated pipe H serves for the admission of hydrogen. Palladium-black or other porous absorptive material forms a layer, C, on a screen above the hydrogen inlet. O shows the charge of oil. In operating this apparatus the layer of material C is first charged with hydrogen and then oil run into the still. Distillation is carried out while hydrogen gas is being forced through the absorptive material and oil.

A peculiar manner of treatment has been shown by Schwoerer,² which will be made clear by Fig. 7. The receptacle A, which is heated by the steam jacket S, is provided with what Schwoerer calls a helical

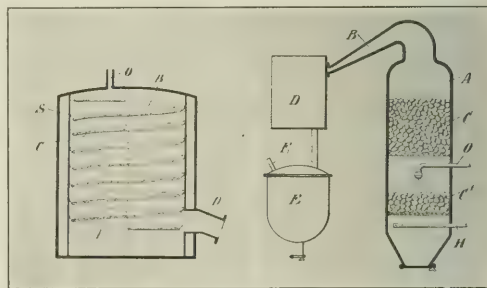


FIG. 7

FIG. 8

pan, shown at B. The underside of the pan carries a layer of nickelized asbestos. O is an inlet for oil and hydrogen, and D an outlet for the treated material.

Schwoerer states that he first mixes fatty acid and hydrogen by atomizing the oil with a jet of superheated steam in the presence of hydrogen and conducts this mixture through the pipe O, into the chamber A. The temperature maintained in the apparatus is from 250 to 270° C. Vapors of oleic acid come in contact with the layer of catalyzer on the underside of the helical pan and are converted into stearic acid. The product collects, more or less, in the gutter of the helical pan and is removed at D.

The repeated caution given by Sabatier to bring in contact with the catalyzer only the vapors of the

¹ U. S. Patent No. 826,089, of July 17, 1906.

² U. S. Patent No. 902,177, of Oct. 27, 1908.

material, doubtless led Schwoeer to devise this form of apparatus.¹

Bedford, presumably with the same caution of Sabatier in mind, discloses, in U. S. Patent No. 949,954, of Feb. 22, 1910, a process which also has to do with vaporization of the oily material. Fig. 8 shows the Bedford apparatus. A still or tower, A, carries two beds of catalyzer, C and C'. This is said to be preferably nickelized pumice. By means of hydrogen under pressure, oleic acid is sprayed from the pipe O, onto the catalyzer bed C'. Hydrogen is admitted through the pipe H. A temperature of about 200° C. and a diminished pressure of about 50 to 100 mm. is maintained in the still or tower A. The vapors of oleic acid mingled with hydrogen pass through the second catalyzer bed C, where more or less conversion occurs, then pass to the condenser D, and finally collect in the receptacle E. F is a connection to a vacuum pump.

Neither this process nor that of Schwoeer is broadly applicable to the treatment of glycerides as these cannot be vaporized without undue decomposition.

Erdmann has taken out a German Patent No. 211,669, of Jan. 19, 1907, involving passing an oil as spray or mist into a chamber containing nickel catalyzer supported on pumice and the like. Fig. 9 probably indicates one form suggested by Erdmann, who, by the way, does not show any drawings in the

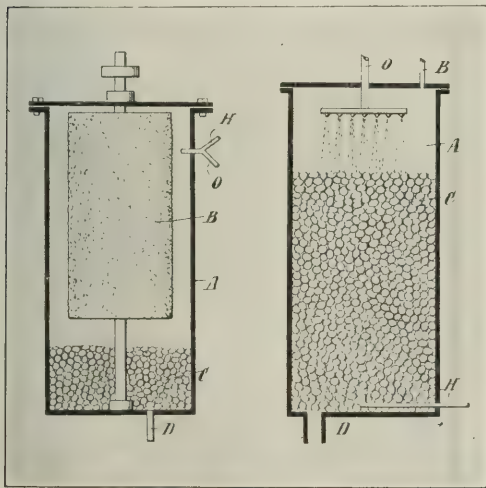


FIG. 9

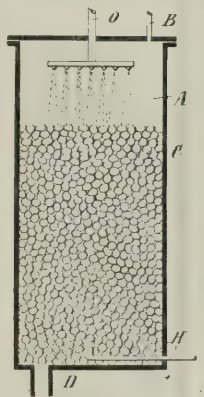


FIG. 10

tating cylinder B, then passes through the bed C, the oil being drawn off at D. The excess of hydrogen is presumably vented in the upper part of the apparatus.

A second modification (Fig. 10) involves a tower, A, filled with catalyzer C, which may be in the form of nickel supported on coarse fragments of pumice. By the pipe O, oil is admitted to the chamber in an atomized or finely divided state. Hydrogen enters by the pipe H. Erdmann states that the temperature of treatment should be from 170 to 180° C. The treated oil is drawn off at D while the excess of hydrogen passes away at B.

In a supplemental patent, No. 221,890, of Jan. 19, 1907, Erdmann recommends the steam distillation from the reaction chamber of the saturated product under diminished pressure.

Vereinigte Chemische Werke A. G.² make use of palladium catalyzer precipitated on an indifferent body as a carrier and recommend as carriers finely divided metals which do not have anti-catalytic properties, also metal oxides and carbonates. Under these circumstances it is stated that one part of palladium is sufficient to convert in a few hours 100,000 parts of oily material to a firm mass. They recommend the use of a hydrogen pressure of two to three atmospheres and a temperature somewhat above the solidification point of the saturated fat. They caution against arsenic, hydrogen phosphide and sulfide, liquid hydrocarbons and carbon bisulfide, chloroform, acetone and free mineral acids as being destructive to the activity of the catalyzer.

Kayser³ describes a process of treating oil with metallic catalyzer consisting in mechanically agitating the oil and catalyzer in the presence of hydrogen, preferably under pressure. One form of the apparatus indicated by Kayser for this purpose is diagrammatically represented by Fig. 11.

Here A is a closed horizontal cylindrical vessel in which is a paddle wheel, D, made up of blades carrying wire gauze. The paddle wheel is rotated

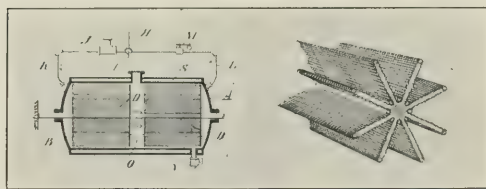


FIG. 11

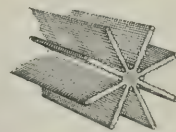


FIG. 12

patent. The chamber A has a rotatable cylinder, B, which is coated with nickel catalyzer. In the bottom of the receptacle is a quantity of nickelized pumice. Oil enters at O and is atomized by hydrogen entering at H. The atomized mixture impinges upon the ro-

¹ Salatiere and Senderens, *Annales de Chimie et de Physique*, [8] 4, 335 (1905), state that "Le métal ne soit jamais mouillé par un afflux excessif du liquide que l'on traite, ou à la suite d'un abaissement accidentel de la température du tube." They further say that in the preparation of cyclohexanol and its homologues from phenol or cresol at a temperature but slightly above the boiling points of the latter bodies, sometimes by their condensation, the nickel becomes moistened and immediately becomes almost inactive, due, no doubt, to the surface becoming permanently changed in character by contact with the liquid phenol or cresol.

by a driving gear at B. In the upper part of the tank is an inlet for charging oil and presumably also catalyzer, the oil being admitted to the tank in an amount sufficient to fill to perhaps one-fourth or one-fifth the entire capacity. Hydrogen is admitted at H and passes, by the three-way cock I, to the compression pump J, going from there to the treating receptacle. At the opposite end of the tank is an exhaust pipe, L, carrying a blow-off valve, M, for the

² German Patent No. 236,488, of Aug. 6, 1910, also English Patent No. 18,642, of 1911.

³ U. S. Patent No. 1,004,035, of Sept. 26, 1911.

with a mixture of hydrogen and oxygen to form hydroxy fatty acids or their glycerides.

Shukoff¹ claims the process of hydrogenating oils by means of nickel derived from the decomposition of nickel carbonyl. Nickel carbonyl may be obtained from reduced metallic nickel by passing carbon monoxide over it at a low temperature. Nickel carbonyl is soluble in oil and is very readily taken up by gases. On heating to a temperature of 200° or so, the carbonyl is decomposed setting free, in a nascent state, metallic nickel which acts as a catalyzer. Shukoff makes use of this reaction of nickel carbonyl by the method indicated by Fig. 16. Carbon monoxide is passed by the pipe G, into the tube B, containing finely divided nickel and the nickel carbonyl formed is conducted to the oil O, which is heated to about 180°. After sufficient nickel catalyzer has formed in the oil, the carbon monoxide stream is cut off, the temperature raised to 220 or 240° C. and hydrogen gas introduced by the pipe H, to bring about hydrogenation.

Day has taken out U. S. Patent No. 1,004,632, of Oct. 3, 1911, supplementing his earlier patent on the treatment of hydrocarbon oils with hydrogen. In the present instance tubes packed with catalyzer are placed in an oil still in such a manner that vapors from the oil may pass through the catalyzer tube in conjunction with hydrogen while being superheated by exterior contact of the tubes with boiling oil.

An English Patent, No. 23,997, of 1909, to Phillips and Bultell, claims to convert mineral oils into oils of lower specific gravity by heating with hydrogen in the presence of nickel or other catalytic agents. They state that the mixture of oil, gas and catalyst may be blown into a heated cylinder and the jet given a gyratory motion either by means of a nozzle revolving about its axis, or by injecting the mixture tangentially to the periphery. In the latter case they state that the cylinder may have an axial core.

The firm of H. Schlinck & Co., of Hamburg, Germany,² hydrogenate oil by passage through a centrifuge, the drum of which carries a porous lining of palladium catalyzer which offers a frictional resistance to the passage of the oil. Fig. 17 shows a centrifugal drum, *a*, which is closed at the top and can be heated. Oil and hydrogen are introduced through the pipe *b*. Openings are provided in the walls of the drum in which is placed rough or porous material covered with precipitated palladium. Several drums may be arranged in series through which the oil may be caused to progress until sufficiently hydrogenated.

Ellis³ uses a stationary catalyzer, filling tubes with the material in granular form and allowing oil to flow through the tubes while passing hydrogen in an opposite direction. Fig. 18 shows a three-section apparatus with the catalyzer tubes *T*, *T*¹ and *T*², heated by the jackets *S S*. Oil from tank *O* flows through the apparatus while hydrogen, admitted by

the pipe *H*, passes through in an opposite direction. The arrangement permits of differential heating so that, for example, the oil may be heated to a temperature corresponding to its particular degree of hydro-

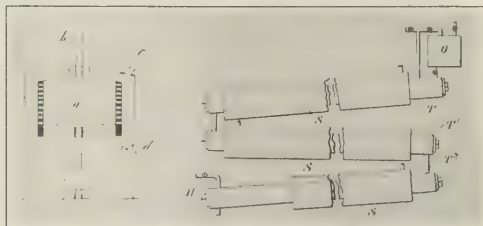


FIG. 17

FIG. 18

genation at any given point, enabling a hydrogenated product free from burnt odor to be obtained. Fig. 19 shows a vertical form of apparatus, the catalyzer being shown at *C* in the tube *A*. Oil is introduced by the pipe *O*, and passes into the tube or cylinder *A*. The pump *P* causes oil to circulate from the top to the bottom of the apparatus through the pipe *B*. Hydrogen gas admitted at *H* is pumped into the bottom of the cylinder *A*, and the excess is withdrawn at the top by the pipe *D*, passing through the drier *E*, and back into the treating cylinder. Oil may be continuously fed through the pipe *O*, in the upper part and the treated product withdrawn at the same rate at the lower part of the apparatus.

In Ellis' Patent, No. 1,040,531, of Oct. 8, 1912, the catalyzer is placed in trays or baskets as shown by

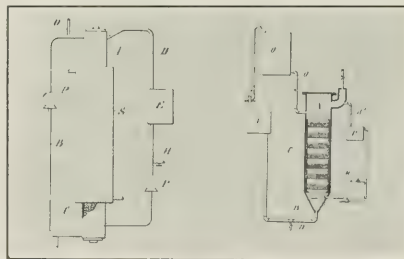


FIG. 19

FIG. 20

Fig. 20 at *C*. The oil travels in a cyclic path downwardly through several layers of catalyzer, and hydrogen gas passes in an opposite direction. Separation of the catalyzer in layers in this manner enables the hydrogen to pass more uniformly through the catalyzer bed. If the catalyzer forms a bed of considerable depth and width, the gas in taking the path of least resistance is liable not to come in contact with some parts of the bed.

The activity of a properly made catalyzer is oftentimes surprising. In the case of a stationary catalyzer we have noted instances of hydrogenation where oil is converted into a hardened fat by momentary contact with the catalyzer.

Fig. 21 shows a photograph of a small laboratory apparatus for testing catalyzer consisting of an in-

¹ German Patent No. 241,823, of Jan. 18, 1910. See also H. Kamps, *Benzenol*, 1912, 1339.

² English Patent No. 8,147, of 1911.

³ U. S. Patent No. 1,026,156, of May 14, 1912.

clined tube containing catalyzer and carried in a heating jacket. Oil is admitted at the right and

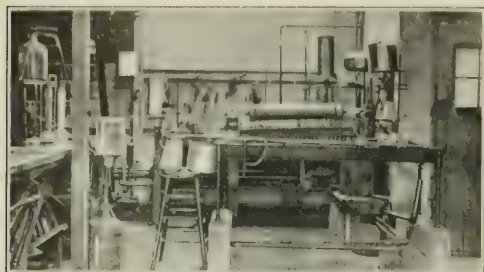


FIG. 21

hydrogen at the left hand end. Fig. 22 shows the catalyzer tube at the right from which extends a horizontal tube supplying hydrogen to the catalyzer tube.

Recently when using a new type of catalyzer we started to pass oil through the catalyzer tube and found hydrogen to be absorbed so vigorously by the oil that instead of passing off through an oil seal at



FIG. 22

the lower end of the inclined catalyzer tube, the oil, curiously enough, was impelled against the strong current of hydrogen passing through the horizontal tube, rushing through it to the point indicated by the hand of the operator (Fig. 22) and there solidifying, actually being well hydrogenated from its momentary passage through the apparatus. A peculiar feature was the advance of the oil from the tube containing catalyzer far into the tube through which only the hydrogen was entering the apparatus. The travel of the oil along the hydrogen supplying pipe in opposition to a rapid current of hydrogen, indicates the possibility of hydrogenating in a very short time, provided a catalyzer of a high degree of activity is secured.

On the other hand, some catalyzers of the nickel and cobalt type when first brought into contact with oil and hydrogen show for a time a marked degree of

sluggishness, but after a period, usually ranging from one to three hours, their activity rather suddenly augments and thenceforth remains apparent for a long period. This sluggishness should not be confounded with the seeming initial inactivity in the hydrogenation of oils containing considerable linolein or other highly unsaturated bodies. In such cases the rate of "hardening" (increase in melting point) is slow at first and later progresses more rapidly. Hydrogenation, in some cases at least, apparently proceeds selectively with initial formation of olein from linolein. Later the olein is transformed into stearin with the observed more rapid increase of titer.

Ellis' effects a constant circulation and contact of the hydrogen gas in accordance with the method shown by Fig. 23. The tank A contains a body oil, O, the space above the oil being filled with hydrogen

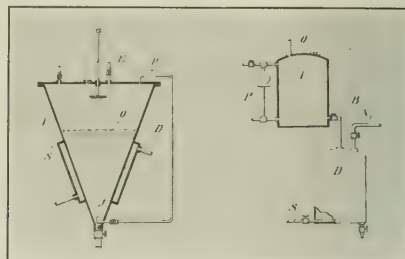


FIG. 23

FIG. 24

under any suitable pressure. The tank is heated by the jacket S. A pump, P, withdraws the hydrogen from the upper part of the tank and impels it through the pipe D, into the lower part of the tank. Catalyzer is added to the oil when the proper temperature is reached and the constant bubbling of a stream of hydrogen through the oil causes intimate contact between the roasting elements. After the operation is completed, the porous plate, fastened to a movable stem in the upper part of the tank, may be depressed to fit into the bottom of the conical base so that when the oil is withdrawn a good portion of the catalyzer remains without exposure to the air and may be used with perhaps a small addition of fresh catalyzer for the treatment of a succeeding charge of oil.

In U. S. Patent No. 1,043,912, Ellis hydrogenates oil (Fig. 24) in the autoclave A. The pump P circulates hydrogen gas through the oil. The treated product is run into the deodorizer D, where it is treated with superheated steam under diminished atmospheric pressure until the oil is freed from noxious gases or vapors. While the deodorization of ordinary cottonseed oil, for example, requires a temperature from 200 to 300° C. and a vacuum of down to one or two inches mercury, the deodorization of the hydrogenated cottonseed oil does not necessarily require as high a temperature and the vacuum "pulled" may be considerably less.²

Contrary to the opinion entertained by many it

¹ U. S. Patent No. 1,040,532, of Oct. 8, 1912.

² See also U. S. Patents Nos. 1,037,881, 1,038,545, and 1,047,013.

does not appear needful to agitate the catalyzer primarily for the purpose of contacting it with hydrogen. Once the catalyzer is wetted with the oil there can no longer be any actual contact with the gas. Hydrogen reaches the catalyzer seemingly only through solution in the oil. The forces of adhesion effectually seal the catalyzer surface from the gas, and no measure of agitation by ordinary mixing apparatus will dislodge the film of oil. Of course, agitation secures the rapid replacement of more saturated by less saturated portions of the oil, but this replacement, under certain conditions, may proceed just as rapidly, simply by diffusion.

CATALYZERS

Catalyzers, those bodies which modify reaction velocity without stoichiometrical participation in the reaction, are destined to find another important industrial application in the hardening of oils.

The previous illustrations show the variety of methods proposed for mingling oil, hydrogen and catalyzer. Among these are several of excellent efficiency. But, after all, the virility, so to speak, of the process, depends on the *catalyzer*. With a powerful catalyzer the hydrogenation of oils becomes a rapid, simple procedure; almost, it sometimes seems, independent of the nature of the hydrogenating apparatus.

Catalyzers recognized as useful for the purpose are nickel and palladium, although platinum, copper, iron and other metals have been used to some extent. Nickel oxide, as stated, has been employed by Bedford and Ipatiew. Wimmer recommends organic salts of nickel such as the formate, acetate or lactate.

As nickel is probably the most important of these catalyzers, in view of its efficiency and relatively low cost, it will be first considered.

The preparation of an effective nickel catalyzer requires considerable care. The oxide or hydrate of nickel is first obtained by ignition of nickel nitrate, or precipitation of nickel hydrate from say a nickel sulfate solution by the addition of an alkali. Obtained in this or in any other suitable manner, the next step is the reduction to metallic nickel. For this purpose the nickel is placed in a receptacle which may be heated controllably, and hydrogen gas is passed over the mass at a temperature ranging from 250 to 500° C. or so, until water is no longer evolved.

The most sensitive catalyzers are obtained by reduction at the lowest possible temperatures. Nickel begins to reduce below 220° C., but at 270° C. the reduction is not complete even after long duration of exposure to hydrogen. A temperature of 300 to 325° C. gives fairly complete reduction and is a satisfactory working temperature. The lower the temperature at which the nickel is reduced, the more sensitive it is to various external influences, hence the preparation of this catalyzer should be conducted not only with respect to degree of activity, but also with respect to longevity.

Nickel is easily poisoned by chlorine and by sulfur in the sulfide form. We have had no unfavorable results from the use of hydrogen gas passed through

a wash bottle containing concentrated sulfuric acid and then conveyed directly to the catalyzer and oil. Traces of the acid were entrained by the gas, but the catalyzer remained in active condition during about two weeks usage under these conditions.

Copper is much less sensitive to poisons than nickel, but on the other hand it is much less active.

Catalyzer made from the oxide without supporting material, weight for weight, is hardly as efficient as when the active surface is increased by the use of a carrier. Hence we find many proposals for the production of catalyzers with a great diversity of carriers, ranging from pumice stone and kieselguhr to charcoal and sawdust.

After reduction of nickel, as above, it should be kept out of contact with air as it is extremely pyrophoric and quickly loses its efficiency on exposure to the air. Consequently when treating oil with such a catalyzer, it is advisable to free the treating apparatus from air by flushing with hydrogen; also it is well to heat the oil and bubble hydrogen through it for a short time prior to the introduction of the catalyzer.

Several methods of producing catalyzers have been the subjects of the patents as, for example, that to Crossfield¹ in accordance with which kieselguhr, asbestos and the like is impregnated with a solution of nickel sulfate and the impregnated material treated with alkali hydrate to precipitate nickel hydrate on the porous material. The product is then well washed, dried and reduced. If kieselguhr is used the powder should contain about 30 per cent. of metallic nickel.

A similar procedure is the subject of a patent to Kayser.² In this case, however, the nickel sulfate or other nickel salt in concentrated solution may be used in an amount to saturate kieselguhr while leaving it in an apparently dry condition, when it is incorporated with a molecular proportion of powdered carbonate of soda and the mixture thrown into boiling water, dried and reduced.

Seeking to overcome the disadvantage of ready oxidation in the air possessed by normal catalytic nickel, Kayser³ reduces the nickel oxide or equivalent material at a temperature of 500 to 600° C. and then passes through the reduced material a brisk current of carbonic acid until the escaping gas proves no longer inflammable. By this method it is claimed that a catalyzer is secured which will remain perfectly cool on exposure to the air and even may be exposed for days without losing any of its catalytic energy.

Wilbuschewitch⁴ proposes to secure more rapid reduction of catalyzer by agitating it in the presence of hydrogen in a heated rotary drum. The temperature during the treatment is stated to be 500° C. Wilbuschewitch⁵ has patented a process of regenerating spent catalysts of the nickel type involving extraction with benzine, treating with alkali solution, acidifying, treating with sodium carbonate solution and reducing.

As a catalyzer in this field palladium has received

¹ English Patent No. 30,282, of 1910.

² U. S. Patent No. 1,004,034, of Sept. 26, 1911.

³ U. S. Patent No. 1,001,279, of Aug. 22, 1911.

⁴ U. S. Patent No. 1,016,864.

⁵ 1,022,347, of April 2, 1912.

considerable study, for, in spite of high first cost, its pronounced effectiveness, together with its ability to effect hydrogenation at relatively low temperatures, makes it particularly attractive.

Many years ago, Fokin¹ stated he regarded palladium as the most powerful of all catalyzers, he having found that reduction takes place readily at 80 to 90° C., while with nickel, a temperature of 180 to 200° C. was necessary for practical hydrogenation. Fokin's experiments at that time were concerned with electrolytic reduction. By this means he reduced linseed, wood, castor and cod liver oil. He found that while palladium-black would reduce oleic acid completely to stearic acid, that platinum-black under the same conditions gave only 24 per cent. of stearic acid.

Paal² worked with colloidal palladium preparations and hydrogenated castor, olive, fish oil and animal fats. He found that sesame oil, after hydrogenation, showed the Baudoin reaction only very faintly, while cottonseed oil no longer responded to the Becchi and Halphen reaction.³ Skita has worked with palladium incorporated with a protective colloid.

Karl⁴ has studied, with considerable care and in a quantitative way, the action of palladium supported on various bodies. He found that palladium precipitated on finely divided nickel or magnesium proved effective catalytically, while if precipitated on lead, aluminum, iron, or zinc, little or no hydrogenation was effected, owing to the anti-catalytic action of these metals. While metallic zinc is anti-catalytic, zinc oxide and carbonate have no such effect. In these investigations Karl worked principally with fish, cotton and castor oil and oleic acid.

HYDROGEN

One of the problems in the hydrogenation field is that of a cheap supply of pure hydrogen. The demand for hydrogen in various directions has increased of late and undoubtedly this will lead to improvement in the manufacture of the gas.

The two methods now most favored in the hydrogenation of oils are the iron sponge steam process and the electrolytic method.

For very large plants the iron sponge steam process is preferred, but it is relatively complicated and scarcely to be recommended for plants calling for 1,000 cubic feet of hydrogen, or less, per hour.

Lane's process is based upon the passage of steam over reduced iron and involves the generation of water gas to reduce and heat the iron oxide employed. For each cubic foot of hydrogen produced, about three cubic feet of water gas are required. The water gas has to be freed from sulfur as otherwise the hydrogen would take up sulfur from the iron sponge and poison the catalyzer. This requires the purification of three volumes of water gas, from which, as stated, a yield of only one volume of hydrogen is obtained.

¹ Chem. Ztg., [2] 1906, 758, [1] 1907, 324.

² Ber., 41, 2282.

³ Paal recommends (U. S. Patent No. 1,023,753, of April 16, 1912) platinum or palladium chloride admixed with a neutralizing agent such as sodium carbonate.

⁴ Inaugural Dissertation, Erlangen, 1911.

The cost of hydrogen made in this manner is about one dollar per 1,000 cubic feet. Fig. 25 shows the process as now installed in the works of a large soap



FIG. 25

manufacturer in England. Figs. 26 and 27 show the Lane process installed at a plant near Paris.

A plant of this type, having a capacity of about 5,000 cubic feet per hour, costs in the neighborhood of \$40,000.

In the electrolysis of brine to make caustic soda and bleach, there exists a by-product of hydrogen sufficient in amount to treat an enormous quantity of oil. To-day a good portion of this hydrogen is allowed to go to waste. Eventually it may be used, to some extent at least, for hydrogenation purposes.

Generators for the production of hydrogen and oxygen by the electrolysis of water are furnished by the International Oxygen Co. One type has an out-



FIG. 26

put of at least 130 cubic feet of hydrogen and 65 cubic feet of oxygen, per day, giving about 7 cubic feet of hydrogen per kilowatt hour. At two cents a kilowatt the hydrogen costs about one-fourth of a cent per cubic foot, if one disregards the value of the evolved oxygen.

The electrolytic process is simple and clean and

is to be recommended, especially for plants of moderate requirements.

We have for some time used hydrogen gas derived in this way and find it suitable for hydrogenation purposes without resorting to any extensive purification.

Abroad, electrolytic cells capable of furnishing hydrogen at high pressure are obtainable, but are very costly.

Very promising methods for the production of hydrogen are: (1) The removal of carbon monoxide and

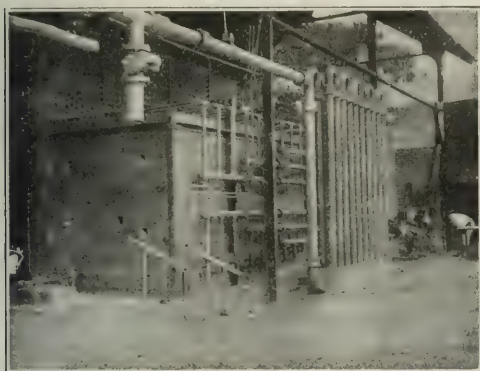


Fig. 27

hydrocarbons from water gas by liquefaction; (2) the decomposition of petroleum at high temperatures; and (3) the passage of water gas and steam at a temperature of 500° C. over lime containing an iron catalyst.

One of the difficulties met with in the handling of hydrogen has been the loss by leakage of the gas. Under pressure and at a temperature of 150 or 200° C., hydrogen is surprisingly penetrating. A treating tank having an oil capacity of about one ton was tested to 150 pounds air pressure and found to be tight, but when hydrogen was introduced at 60 pounds pressure, the leakage was tremendous.

A stuffing box tested at 120 pounds steam pressure emulated a whistle, with hydrogen at *one-half* the steam pressure. Autoclaves with welded seams are desirable for high pressure and high temperature work. Moving parts should be avoided as far as possible.

USES OF HYDROGENATED OILS

The ability to prepare from ordinary *liquid* fatty oils a fatty body of almost any desired degree of consistency renders hydrogenation especially attractive in the production of edible fats and soap-making materials. These are, undoubtedly, two of the most important applications, although hydrogenated oils are likely to have rather wide use in the arts. In the manufacture of lubricants, for example, the hydrogenated fats may be used to advantage.

HYDROGENATED OILS IN THE SOAP INDUSTRY

By hydrogenation, oils which formerly made soaps only of soft consistency, now yield the more valuable hard soaps. This has led to a very rapid development of the art with respect to the production of soap-

making fats. In particular, fish and whale oils have been made use of, because these oils may be completely deodorized by the addition of hydrogen.

According to a Japanese chemist, Tsujimoto, the odor of fish oil is due almost entirely to a fatty constituent and not to so-called impurities. This fatty constituent is clupanodonic acid having the formula $C_{18}H_{32}O_2$, which, therefore, by the addition of 8 hydrogen atoms, becomes stearic acid. When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent. Even the fishy taste is scarcely in evidence.

For soap-making, this product is satisfactory as it complies with the test for a deodorized fish oil suitable for soap-making in that the odor of the original oil is not apparent when ironing laundered goods on which such soaps are used. If, however, the hydrogenation is not carried on to a point where the iodine number is approximately 50 or less, there is some danger that the fishy odor will become apparent during the ironing operation.

Crossfield & Sons¹ have patented, in some countries, the use of hydrogenated oil in the manufacture of soaps. They claim the hardened or hydrogenated fats have the advantage that a weaker brine suffices to separate the soap from the glycerine; further, that the soap produced from such hydrogenated fats is exceedingly hard; as, for instance, soap made from hydrogenated cottonseed oil is stated to be about 12 times as hard as that made from untreated cottonseed oil. This, of course, enables the admixture of a larger proportion of rosin, which naturally would be looked upon as a decided advantage.

In contrast to this, a German writer² states that the hardened oils form soaps which are too hard to give good lathering properties.

Since soaps are made almost invariably of mixtures of fats, it is under the control of soap-makers to use such an amount of hydrogenated fat as would give the requisite degree of hardness without sensible diminution in lathering power; hence the foregoing criticism seems to be without great weight.

It suffices to state that hydrogenated fats for soap-making purposes are being made abroad by a number of firms and are giving good satisfaction in many instances. The Germania works at Emmerich, Germany, offers on the market three grades of hardened oil.

In this country satisfactory results are being obtained commercially in the manufacture and use of hydrogenated oils in soap-making. Several plants are operating or planning to operate on the large scale.

EDIBLE HYDROGENATED OILS

Since the addition of less than 1 per cent. of hydrogen suffices to convert cottonseed oil or other vegetable oils into a fatty body of the consistency of lard, it follows that manufacturers of ordinary lard compounds (that is to say, a mixture of 80 to 85 per cent. of refined cottonseed oil and 15 to 20 per cent. of oleo-stearine) have promptly turned their attention

¹ English Patent No. 13,042, of 1907.

² *Seifensieder Ztg.*, 39, 660.

to the production of the compound by a "self-thickened" cottonseed oil.

The high cost of oleo-stearine makes the method an attractive one and the hydrogenated product from cottonseed oil has the advantage, if properly made, of being very stable in character.

We believe, however, that for best results, it is desirable to hydrogenate the entire body of oil to a fatty acid titer of 36 or 38, or whatever consistency may be required, rather than to take 20 per cent. or so of the oil and harden it to a titer of 52 or thereabouts and incorporate with unhydrogenated oil.

It appears that the hydrogenation of the total body of the oil, by transforming the linoleic and linolenic compounds and the like, has a tendency to improve the oil as regards its edibility and certainly gives it greater stability.

EDIBILITY OF HYDROGENATED OILS

It seems to be generally accepted by those who have investigated the matter carefully that the hydrogenated oils have as desirable a degree of edibility as the oils from which they are derived. It is even claimed that by destroying traces of certain unsaturated bodies thought to be slightly toxic in nature, hydrogenation renders the oil better adapted for human consumption.

A question of serious import has, however, arisen in the use of nickel catalyzer. Aside from the fact that by careless filtration, traces of the suspended nickel may be present in the product, there is the more serious problem of the actual solution of nickel to form nickel soaps which cannot be easily removed.

According to Bömer,¹ nickel is dissolved by oils during the hydrogenation treatment only when the oil contains free fatty acid in considerable amounts. A sample of hydrogenated sesame oil containing 27/2 per cent. of fatty acid was found to contain 0.01 per cent. ash with 0.006 per cent. nickel oxide. Whale oil, containing 0.6 per cent. fatty acid, yielded 0.006 per cent. ash and 0.0045 per cent. nickel oxide. Such an amount of nickel presumably would not be tolerated in a product intended for edible purposes.

The Bureau of Animal Industry of the Department of Agriculture is now investigating the matter and apparently intends to determine the relative degree of toxicity of the traces of nickel in the form existing in improperly made hydrogenated oil. We may add that, so far as can be ascertained, the Department looks kindly upon the advent of hydrogenated oil in view of the likelihood that it is destined to prove a very acceptable substitute for higher priced animal fats and does not propose, according to my understanding, to venture any ruling until the matter has had protracted scrutiny.

It is our belief that the use of nickel in the form of an oxide, or the use of nickel catalyzer containing more than traces of oxide, is undesirable from the point of view of solubility in oil. Nickel, in the metallic state, cannot combine with a fatty acid to produce a soap, except with the elimination of hydrogen, and in the presence of an atmosphere wholly of hydrogen,

because of mass action, such reaction would not be likely to take place. On the other hand, nickel in the form of oxide would yield water on combining with fatty acid which would be yielded practically into a vacuum as regards the vapor pressure of water.

Hence it seems to the writer that in the manufacture of products intended for edible purposes, care should be taken to maintain conditions such that the catalyzer, if of the nickel type, is preserved almost wholly in the metallic state. Also it is desirable to not force the reaction too rapidly with the consequent danger of breaking down the carboxyl group and setting free water which would react to produce fatty acid.

Finally, it may be stated, by partial saturation of glycerides, we have the possibility of preparing from tri-olein the oleo-distearine or the dioleostearine. Dioleopalmitin would give either oleostearopalmitin or distearopalmitin. From tri-olein we may have the two isomeric oleo-distearines, α - and β -oleo-distearine as well as α - and β -dioleostearine. Which of these we may be able to produce controllably and which may prove best from the edible standpoint are problems for the future to solve.

MONTCLAIR, N. J.

BORON: ITS PROPERTIES AND PREPARATION¹

By E. WEINTRAUB

To the study of the chemical elements attaches a twofold interest. Their differences and similarities are a constant source of speculation, and any increase in the knowledge of their properties is an advance toward the discovery of the underlying laws of the constitution of matter. To the practical man the elements have the still further interest that they may have some unusual properties capable of technical application. All would like to learn the properties of such elements as uranium, titanium, and a number of others, and to know what they are good for.

The element boron is interesting from both points of view. It has exceptional characteristics—characteristics almost unique among elements, and it is also capable of practical uses of considerable importance.

In an article published in the 1909 Transactions of the American Electrochemical Society, Vol. 16, p. 165, the methods for the isolation of the element boron and the main properties of the element were described. The work has been going on steadily since then, mainly in the direction of developing the practical applications.

SPECIFIC RESISTANCE OF BORON

Among the characteristics of boron, the most interesting are those pertaining to its electrical resistance. The specific resistance of pure fused boron at ordinary temperature is very high, as compared to that of other elements which have any appreciable conductivity at all. Thus a piece of boron, regular in shape, two one-hundredths of a centimeter long and two one-hundredths of a centimeter square in cross section, has a resistance at 20° C. of nearly two and a half million ohms, or, in other words, 10¹² larger than

¹ Abstracted by W. R. Whitney from a lecture presented by Dr. Weintraub before the Eighth International Congress of Applied Chemistry, New York, September, 1912.

¹ Chem. Rev. Fett.-Harz.-Ind., 1912, 221.

that of copper at ordinary temperatures. The element silicon, which comes next to boron, in resistivity, is still separated by a very considerable gap from it. The specific conductivity of boron at 0° is equal to about $0.5-0.6 \times 10^{-6}$ reciprocal ohms per cm./cm²., the conductivity of silicon is 1.8, or nearly a million times as large as that of boron.

NEGATIVE TEMPERATURE COEFFICIENT OF RESISTANCE

This high specific resistance of boron is accompanied by a negative temperature coefficient of resistance, which is also unprecedented among elements. The resistance of boron drops very markedly as the temperature is increased, and it does this with exceptional rapidity at ordinary room temperature. At this temperature the conductivity of boron doubles in value for every seventeen degrees centigrade, as is illustrated by Fig. 1, where the temperature interval is $27^{\circ}-450^{\circ}$ C. The change in resistance is so great that it is difficult to represent the measurements on one curve, so two curves are used. In the first one the temperature interval is $27^{\circ}-200^{\circ}$ C. and the unit of resistance is a megohm; in the second one the tem-

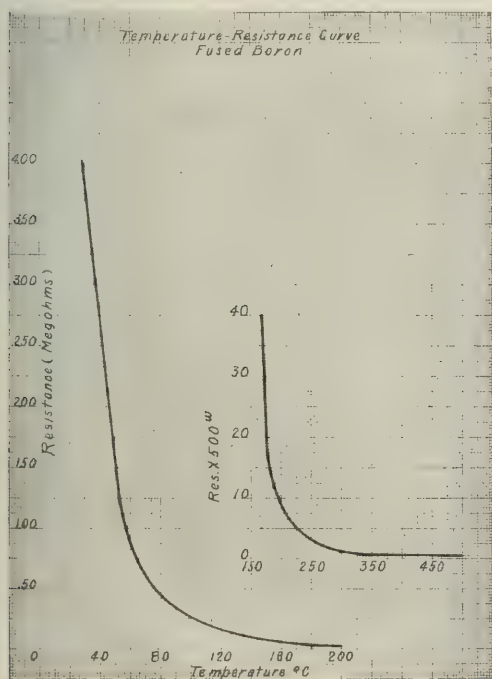


FIG. 1

perature interval is $200^{\circ}-450^{\circ}$ C., the unit of resistance is 500 ohms.

The following table gives measurements made on a very small piece of boron, which are plotted in Fig. 2.

Three ordinate scales are used, the resistance units being 10,000, 1,000 and 50 ohms, respectively, and the total temperature interval is room temperature to 650° C.

The cold resistance is 9,000,000 ohms and the re-

sistance at 650° is too small to be represented even on the smaller scale of the last curve. At tempera-

Temperature Degrees Centigrade	Resistance Ohms
27	775,000
100	66,000
170	7,700
320	180
520	7
600	4

tures above 1000° the resistance is but a fractional part of an ohm.

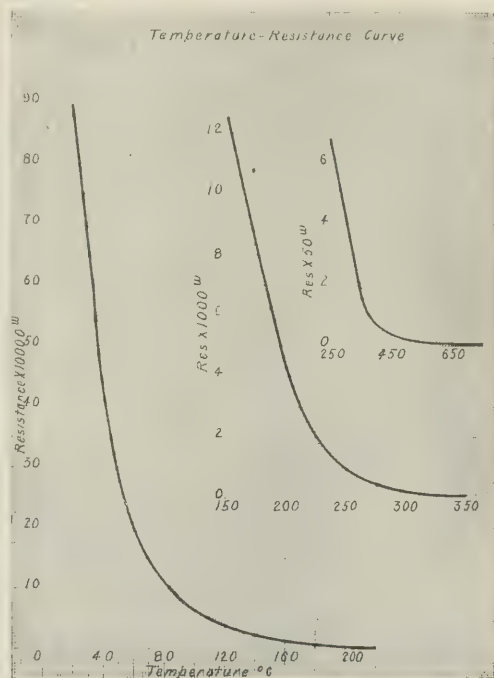


FIG. 2

The relation between temperature and resistance is not a simple one, but for small intervals of temperature it can be assumed that the drop in resistance is proportional to the resistance and the change in temperature, that is,

$$\Delta R = -\alpha R \Delta T.$$

At ordinary temperature the temperature interval, for which the resistance drops to half value is, as stated above, about 17° ; this interval of temperature increases as the temperature rises, and at 600° it is about 80° . This leads to an exponential expression for the resistance which can be used for small intervals of temperature of about 50° with only a small error.

A comparison of this behavior of boron with that of other materials is instructive. It is generally known that metals have a *positive* temperature coefficient of resistance; in other words, their resistance increases with temperature. The metalloids have a negative temperature coefficient of resistance. Carbon, in its

amorphous form, has a slight negative temperature coefficient, its resistance dropping in the ratio of two to one between ordinary temperature and white heat. Silicon again comes nearest to boron, but the gap separating the two is again very considerable. Resistivity measurements on specimens of chemically pure silicon have never been made. It is, moreover, difficult to make consistent measurements on silicon on account of its tendency to crystallize in grains of different size and shape, but some specimens will show a drop of resistance as large as one hundred to one between ordinary temperature and the temperature near its melting point, which is about 1400°C .

Roughly speaking, therefore, between 0° and a good red heat the resistance ratio is for carbon, two to one, for silicon, one hundred to one, and for boron 10^6 or 10^7 to one.

Among compounds there are a large number with negative temperature coefficients of resistance. A familiar example is the Nernst Glower, which is a mixture of oxides and shows a very great drop in resistance with rise of temperature, which drop, however, begins, or at least becomes measurable only at high temperatures, 500° to 600°C . The same holds true for pure oxides. The drop of resistance of calcium oxide and of copper oxide from measurements made by Horton, are given in the following tables:

	Temperature	Resistance
Calcium oxide.	763°	7×10^6
	1011	2×10^6
	1468	91
Copper oxide.....	12	462,400
	59	91,560
	134	12,360
	1038	0.02

While calcium oxide shows a drop of resistance only at high temperatures, copper oxide shows a rapid drop of resistance around room temperature, and in this way is very similar to boron.

The element boron then approaches in its electrical behavior more nearly certain compounds than the elements. As was pointed out in another place, it is the magnitude of resistance that determines the sign and value of the temperature coefficient of resistance and no fundamental difference exists in that respect between elements and composite substances.

Fig. 3 shows the relation between the resistance of boron and the watt input. This curve has not the theoretical importance of the temperature resistance curve, but is useful in connection with practical applications. The general course of the curve is the same as that of the temperature-resistance curve. The drop of resistance with watt input is so rapid that it is hard to represent it on one scale even with such a small variation of wattage as is embraced by the curve, namely, between 7 and 28 watts. The curve refers to a small piece of boron in air.

INFLUENCE OF DISSOLVED ELEMENTS

The influence of the addition of other elements dissolved in boron is no less interesting. This influence is of extraordinary magnitude, so that even as small an amount as 0.1 per cent. of carbon, for instance, will increase the conductivity of boron many fold.

When 7.8 per cent. of carbon are dissolved in boron the remarkable characteristics of boron disappear altogether and the material has a conductivity comparable to that of silicon or even carbon. The law of variation of the conductivity of carbon with the content of dissolved material is not established, but the experiments, as far as they have been carried out, point to an exponential curve. These experiments are as difficult as they would be interesting. One of the difficulties is the necessity of very accurate chemical analysis as a small error in the analysis would produce an enormous change in the curve.

It is again interesting to compare this behavior with that observed in other substances.

With metals the opposite case is true; if one metal is dissolved in another the resistivity increases, not

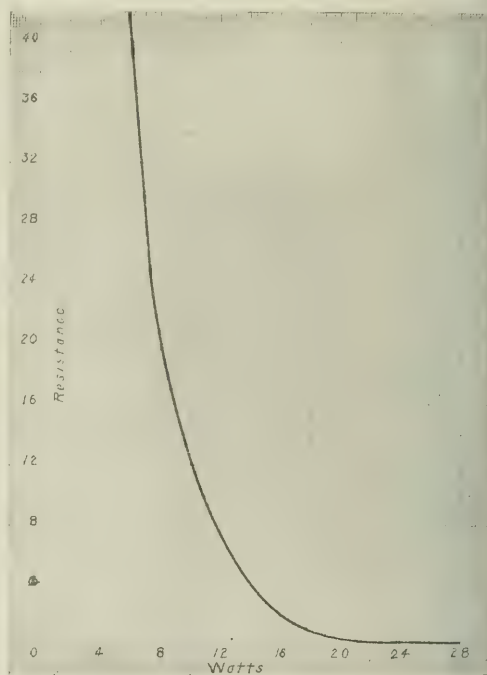


Fig. 3

the conductivity. Silver is a better conductor than copper, but addition of silver to copper increases the resistivity of the latter. With "poor" conductors, however, the conductivity of mixtures is greater than that of pure substances. This general behavior of poor conductors has been pointed out by the author previously.

Hand in hand with this diminution of resistivity goes the decrease in the value of the temperature coefficient of resistance. The temperature coefficient of resistance of solutions of elements in boron is still negative, but less so; so that while the difference in specific resistance at ordinary temperatures between boron and its solutions is very great, this difference becomes less and less as the temperature increases.

Finally, at high temperatures, in the neighborhood of 1000° there is very little difference in the conductivity of boron and the conductivity of dilute solutions of other elements in boron; all the resistance temperature curves seem to come together at high temperatures.

The reverse phenomenon has been observed with metals, but leading to the same final result. A solution of silver in copper is a poorer conductor than copper, but the temperature coefficient of resistance which is positive in this case is smaller than that of copper. At high temperatures the two curves will probably come very near together.

The rise in resistance, which takes place with good conductors, the drop in resistance which takes place in poor conductors, the above-described connection between the temperature coefficient and the magnitude of resistance all suggest the possibility that at a certain very high temperature all materials if preserved in solid or liquid form would show the same conductivity. What the value of that temperature is and what the theoretical significance of it may be are questions which will not be discussed here.

For the practical use of boron this influence of dissolved substances is very important, because one has it in his hand to change the specific resistance within very wide limits and also to change the temperature coefficient from the enormous value it has in boron to a very small value.

VOLT-AMPERE CURVE AND BREAKDOWN VOLTAGE

A consideration of the nature of the curve representing the relation of the current and voltage across a piece of boron is of importance. The volt-ampere curves of solids have not been used very much in theoretical discussion, for the reason that they have not the fundamental importance of the tempera-

ture resistance curve. These curves have, however, been used in the study of gaseous discharges to a great extent (Kaufman) for the simple reason that in this case the volt-ampere curve is the only thing that can be determined. In the study of the volt-ampere curve of solids or liquids three cases can be distinguished (see Fig. 4). If the resistance does not vary with the temperature, then the volt-ampere curve is a straight line and the tangent is a measure of the resistance (Curve I). For a material with a positive temperature coefficient of resistance (metals, etc.) the curve will be convex to the axis of abscissa (Curve II); in some cases when the temperature coefficient is large enough a part of the curve may run almost parallel to the axis of ordinates (Curve III). In other words, there may be a region in which a very large variation in volts corresponds to a very small variation in the current. This case is exemplified by iron, within a certain narrow interval, and also by tungsten. Placing these materials in hydrogen is favorable to this result, as the heat dissipation (conduction) at lower temperature is relatively more favored than at high temperatures (mostly radiation). For a material with a negative temperature coefficient the general form of the volt-ampere curve is represented by Curve IV. The resistance corresponding to 0 current is represented by the tangent of the angle and the whole curve will lie between this tangent and the axis of abscissae. This is because the volts rise more slowly than if the resistance remained constant. A few simple considerations will show that the curve will, in general, possess a maximum. From $E = RI$ it follows that

$$dE = RdI - I[dR].$$

$[dR]$ indicates the absolute value of the resistance change. For $I = 0$ one has, of course,

$$\frac{dE}{dI} = R.$$

For low values of current dE is represented essentially by RdI which is positive; therefore, the voltage first increases with the current. However, as the current increases the second factor, $I[dR]$ becomes more and more important; since the first factor containing R becomes smaller as the resistance drops, a point is finally reached where the two are equal. At this point $dE = 0$ and the voltage is a maximum. From this point on, $I[dR]$ will predominate and the volts will drop with increasing current. The general form of the curve is, therefore, that given by IV. It is seen that for the same value of voltage there correspond in general two values of current and that the curve consists essentially of two different parts, a rising part in which the conditions correspond to stability and a falling part which is essentially unstable. On this falling part no equilibrium is possible (unless there is external resistance in the circuit with a constant or rising characteristic). On constant voltage the current and the energy input (represented by the area of the curve) would increase until a condition equivalent to a short-circuit would take place. The point M which separates the two branches of the curve and which corresponds to the maximum voltage possible

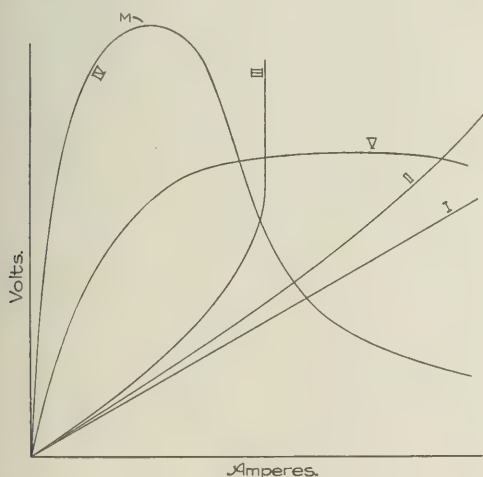


FIG. 4

ture resistance curve. The temperature resistance curve is perfectly definite; the volt-ampere curve will vary with the way in which the heat is dissipated. This is because a certain volt-ampere product means a certain watt input which may give any temperature

across the resistor will, on this account, be called the "breakdown" voltage.

It is at first sight somewhat difficult to see why the breakdown does not occur with ever so small a voltage since the energy introduced into the resistor should cause a drop in resistance; this in its turn causes an increased energy input, and so on. It will, therefore, be instructive to derive the existence of a breakdown point on the basis of energy relations. It will suffice to consider the very simple case in which constant voltage is applied, E . The energy input is equal to

$$W = \frac{E^2}{R},$$

and assuming that R is an exponential function of the temperature the energy input has the value

$$W = \frac{1}{C} E^2 e^{\alpha T}$$

If the temperature at which the breakdown occurs is low (this is true of boron), one may assume that the dissipation of energy takes place only by heat conduction and therefore is proportional to the temperature difference and is equal to AT . At equilibrium, energy input and output must be equal. Hence, equation

$$\frac{E^2}{C} e^{\alpha T} = AT.$$

By simple reasoning it is easy to see that this equality is possible only when E is below a certain critical value. When the volts exceed this critical value the equality is no longer possible at any temperature and the input will always be larger than the output. This particular voltage will correspond to the breakdown voltage. If the breakdown occurred at higher temperatures, the second part of the equation would contain a term corresponding to radiation, but the general conclusion would not be changed. Nor will it be materially affected if the resistance-temperature function is not exactly exponential.

The form of the curve discussed up to the present is characteristic of boron itself and all similar materials which have a very large negative coefficient of resistance. According to the value of this temperature coefficient and also to the values of the constants C and A (nature of the surface, of heat insulation) the curve may assume different forms. After the maximum voltage corresponding to M is reached the voltage may drop only very slightly or move along a horizontal part giving a constant voltage with varying current (Curve V) and finally the maximum voltage may lie at very high temperatures so that the falling part of the curve is not reached at all in ordinary work. In this case the curve is constantly rising, always remaining concave toward the X axis. The same form of volt-ampere curve may be obtained by combining a resistor with a positive temperature coefficient and one with a negative temperature coefficient of resistance, in series or in multiple.

These theoretical conclusions are illustrated by the following curves which are the result of actual measurements made on boron and on boron with a small percentage of carbon. Fig. 5 gives a volt-ampere curve obtained from measurements on a small piece

of pure boron in air. The contents were made by fusing on platinum wires. The first part, from 0 up to the maximum, rises very rapidly. The tangent of the angle this part forms with the axis of abscissa, gives the resistance of the material at room temperature. At 400 volts the breakdown voltage is reached.

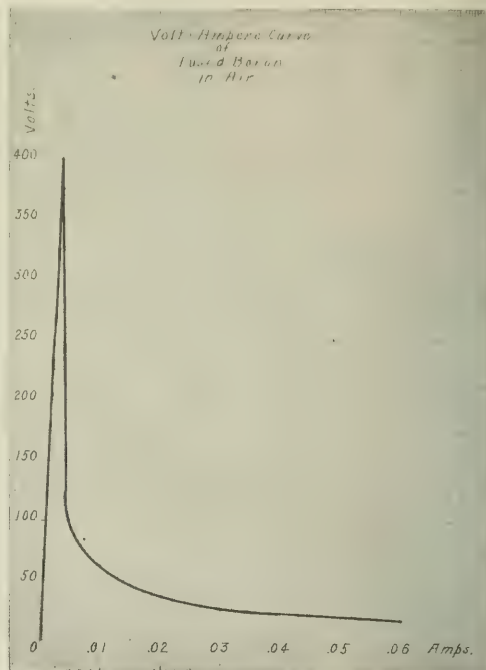


FIG. 5

The current corresponding to this part is only about 0.004 of an ampere. After the breakdown occurs the current rises and the voltage drops very rapidly.

In Fig. 6 the same measurements are represented but the part of the curve around the breakdown point is shown on a different scale.

Fig. 7 shows the volt-ampere curve of boron containing a small percentage of carbon. The breakdown voltage is lower, only about 80 volts in this particular case, but the general course of the curve is the same, except that the whole curve is lower.

Fig. 8 shows the time interval before the material breaks down at different impressed voltages. With this particular piece the breakdown voltage is about 85. As the voltage is gradually raised above this value the material breaks down after an interval which is the smaller the higher the voltage applied, until at 140 volts the breakdown is practically instantaneous.

OTHER PROPERTIES OF BORON

Boron is very hard. That would be expected, from the fact that boron carbide is a very hard material. Moreover, both boron and boron in which small percentages of other elements are dissolved can be prepared in a form in which they are tough to a certain extent, and in that way they differ from carborundum and

other artificial hard materials. The combination of these properties make possible their use for small bearings, such as meter jewels and for similar applica-

perfect polish. These methods have now been developed and meter jewels obtained, a large percentage of which are equal to diamond as to life and as to constancy of friction.

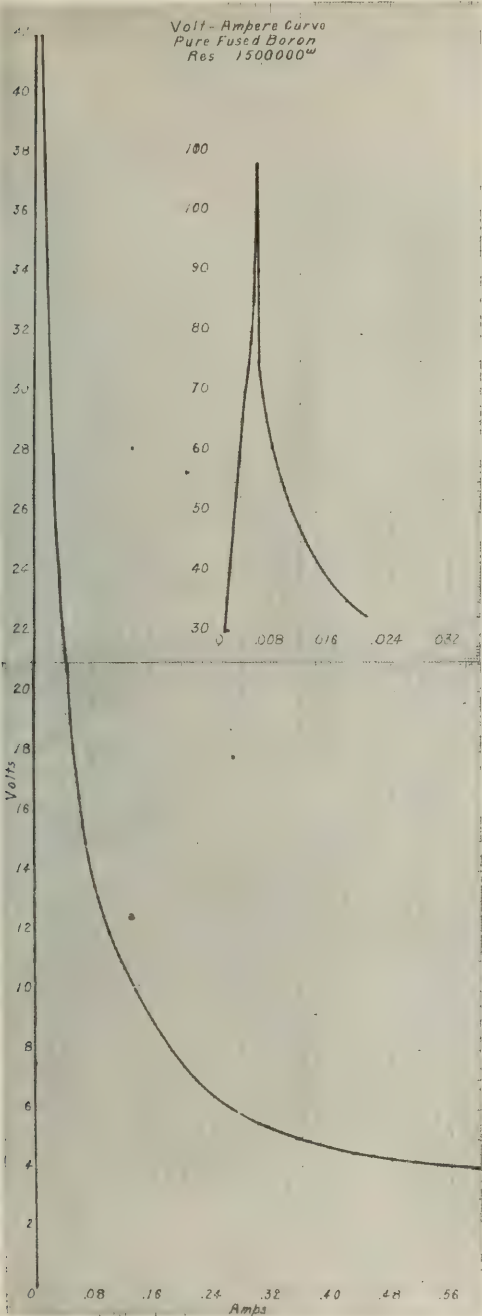


FIG. 6

tions. It has been, however, necessary to develop methods which would make a perfectly homogeneous material devoid of porosity and capable of taking a

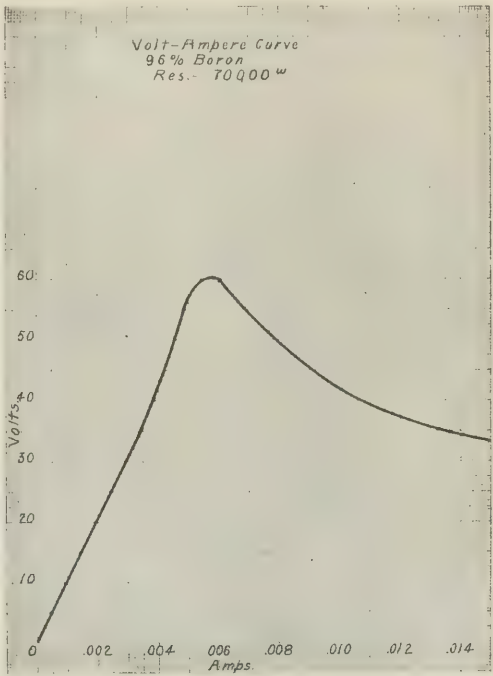


FIG. 7

CAST COPPER

Boron sub-oxide, a by-product obtained in the manufacture of boron, can be used for obtaining high conductivity cast copper. Copper cast without additions is full of pores and blow-holes, and therefore, mechanically unfit and of very low electric conductivity; the removal of the gases from copper by the known deoxid-

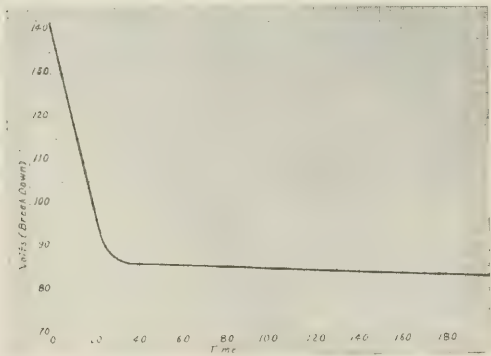


FIG. 8

izers is liable to give an alloy containing a small amount of deoxidizer, an amount sufficient, however, to lower the conductivity of the copper very consid-

erably. Boron sub-oxide, however, has the property of deoxidizing copper without combining with it, as boron sub-oxide has no affinity for copper. Tons of copper are cast now by this process, improving the quality of the product and at the same time cheapening it.

METHODS OF PREPARATION OF BORON

A brief description of the methods used to produce pure fused boron, also technically pure material in quantities, and to bring boron into definite shape, may be of interest. The methods are novel to a large ex-

Electrochemical Society, Vol. 16, p. 165 (Oct., 1909). This boron sub-oxide or magnesium boride compound is decomposed and the resulting boron melted in an arc. As boron sub-oxide is practically an insulator a high potential arc is used. Boron sub-oxide in a copper cup forms one electrode, the other is formed by a water-cooled copper electrode. The fusion takes place in an indifferent atmosphere, such as hydrogen. The arc is started with the two electrodes a certain distance apart by means of a high voltage, say 15,000 volts, delivering a relatively small current; when every-

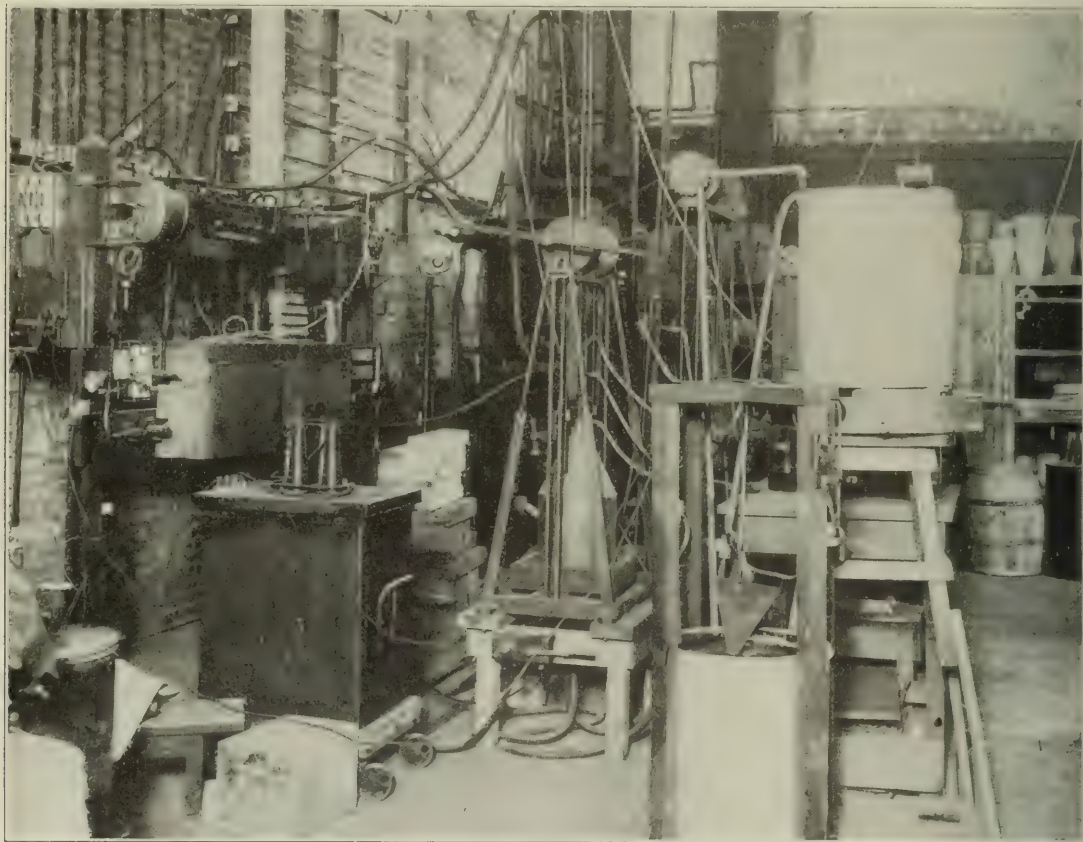


FIG. 9

tent and once developed in case of boron have shown themselves capable of applications in other fields.

The starting point in the preparation of technically pure boron is the reaction which has been studied before, the reaction between boric anhydride and magnesium or alkali metals. This reaction gives different products according to the relative weights of the substances employed, the temperature, and so forth. One interesting product obtained under certain conditions is boron sub-oxide of the approximate formula B_2O_3 . Under other conditions a product consisting of boron and magnesium boride is obtained. Detailed description of this reaction can be found in the article of 1909, in the *Transactions of the American*

thing is heated up the voltage is changed to about 2200 volts, the current to 50 amperes. After a while it is possible to reduce the voltage to 500 volts D. C. and increase the current to the desired value; by using 200-300 amperes it is possible to melt down a few pounds of boron at once.

Fig. 9 shows the small furnace used for some time but now replaced by a much bigger one. In this size of furnace only about a pound of boron can be melted in one operation. The iron hood can be moved up and down and through it hydrogen is flowing. Inside is a water-cooled copper cup containing the boron sub-oxide powder. Through the top a water-cooled copper terminal passes and is insulated from the hood.

A window is provided through which the operation of the furnace can be watched. The high voltage transformer and busbars conveying 2000 volts—(50 amperes and 500-700 volts—300 amperes, respectively)—are shown to the left of the furnace.

In this way it was found at first impossible to make absolutely pure boron. As long as the impurities are boiling out of the boron there is no danger of contamination with the material of the upper electrode; but when the state of purity of boron is approached the danger becomes considerable, and one has to stop a little short of absolute purity. With great care a material can be obtained containing about 99 per cent.

purposes they are apt to contaminate the material to be treated. They do not give a clear heat, that is, high temperature and nothing else. The new furnace is based on the use of a mercury electrode. It is a mercury arc furnace in an indifferent atmosphere.

Another method for making boron was developed before this one, and is capable of giving absolutely pure boron but is not as well adapted for producing large quantities. This method takes for its starting point boron chloride. If boron chloride is brought together with hydrogen at a high enough temperature it is reduced to boron and hydrochloric acid. All the materials taking part in the reaction are gaseous

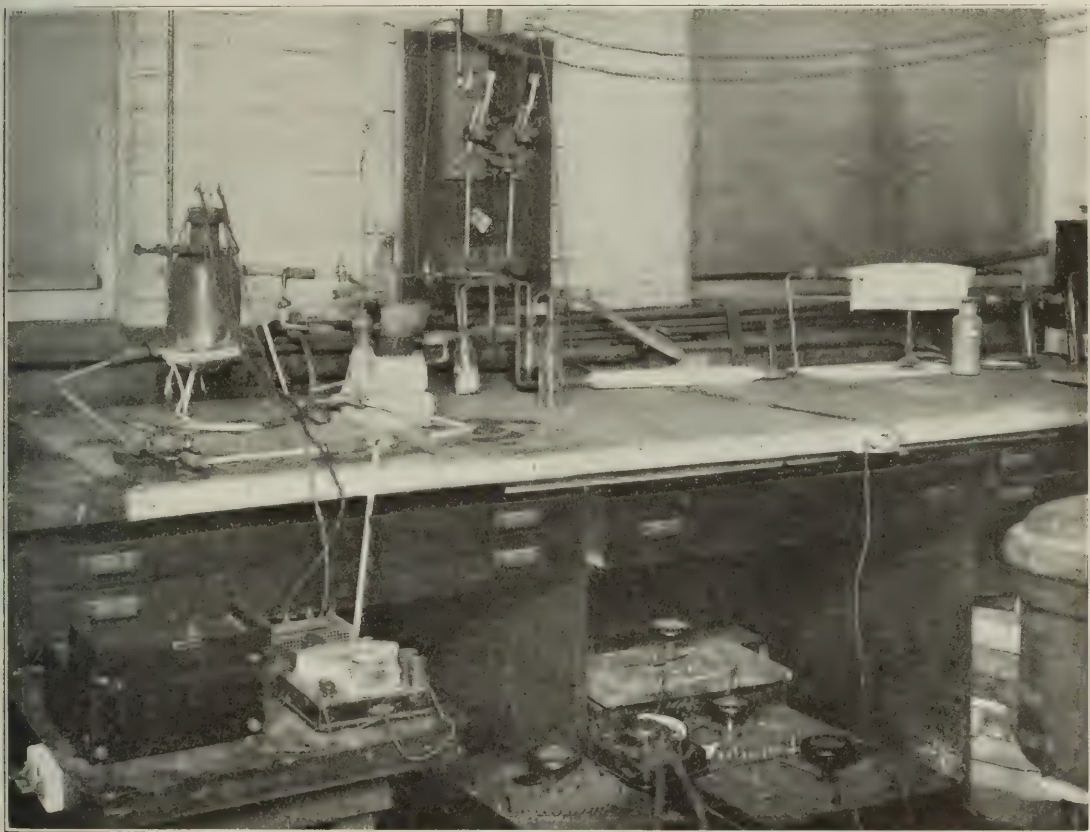


FIG. 10

boron. The average product will perhaps be not more than 97 to 98 per cent. boron. This product is good for some applications, but not for others.

It was necessary to develop an arc furnace in which no impurities at all would be introduced, either by chemical combination or mechanical admixture of the product of disintegration of the cooperating electrode. This has been accomplished and a furnace has been constructed in which practically any material can be melted down without introducing the slightest impurities into it. Most of the known arc furnaces use carbon electrodes or water-cooled metallic electrodes, and while they are excellent for some

except boron itself. As boron chloride can be made very pure and the slight impurities that may be in it are not reduced by hydrogen, the product is chemically pure boron in the most accurate sense of the word. If boron in the form of powder or lumps is wanted the reaction is carried out in an arc discharge between copper, or better, boron terminals. For practical applications (for making regulators, cut-outs, meter jewels) where a deposit of boron is wanted the gases are passed into a vessel in which a filament or plate is brought to incandescence by current.

The apparatus used is shown in Fig. 10. The hydrogen, freed from oxygen and dried in the usual way,

passes through liquid boron chloride which is kept at a definite temperature and the mixture passes then through the vessel on the left, where it is caused to react by the incandescent body. The procedure is modified in case it is desired to deposit a definite amount of boron. A vessel of definite dimensions is then filled with boron chloride and hydrogen of definite pressure.

SHAPING BORON

The arc furnace delivers irregular lumps of boron. Starting with these, the problem is to make a rod of boron. Casting in a mold is excluded because the

material is to be used for the envelope. The temperature must be high around 2300° . At that temperature the material must not have an appreciable conductivity or else it would take current itself, but above all it must not attack boron. Boron is very active at high temperatures and attacks practically everything known, all oxides included. The solution of the difficulty was found in the use of a boron compound—boron nitride, a substance described in all books of chemistry, but whose physical properties have not been well known. It is infusible, even at the temperature at which tungsten melts. More than



FIG. 11

melting point of boron is about 2300° C. It was found impossible to agglomerate the very hard boron by mere compression. The use of binding material would introduce impurities; but even if the material were agglomerated, the subsequent sintering by current would be a difficult matter on account of the large negative temperature coefficient resistance of boron. The current has a tendency to concentrate in lines which happen to have a higher conductivity; streaks develop, causing melting through in points before the whole mass is sintered. It was necessary to surround the boron with an envelope which would equalize the temperature and preserve the shape. But what ma-

terial, boron nitride is a very poor electrical conductor at high temperatures, much poorer than any other known insulator. For instance, a small disc of magnesium oxide $\frac{1}{8}$ inch thick passed in some of the tests an appreciable current at 800° C. with 110 volts applied. A disc of boron nitride of the same dimensions heated at 1200° C. and put across 500 volts gave no measurable current. These two properties, infusibility and high insulating power at high temperatures, make it the ideal substance for an envelope in sintering boron. One more thing is necessary in order to make the sintering furnace complete; it is necessary to insure good contact between

the boron powder and the electrodes which conduct the current to it. This was done by applying pressure, and so a new type of furnace was developed, the "boron nitride sintering furnace." With this furnace not only boron, but also boron carbide, tungsten, and a large number of other materials have been formed into rods. On account of the inertness of boron nitride almost any refractory material can be sintered in this furnace, and it is difficult at present to foresee all the possibilities of this furnace in the direction of sintering materials or combining materials at elevated temperatures under high pressure.

Of course, in order to use boron nitride in this furnace, methods had to be developed for making boron nitride relatively cheaply and in large quantities. Fig. 11 shows a small size boron nitride furnace.

Due credit is given to the men of the West Lynn Research laboratory of the General Electric Co. who ably assisted in this work—G. Weintraub (work on the arc furnace, on the boron nitride furnace, etc.), H. Rush (designing of boron nitride furnace), E. Kraus (boron chloride reaction), F. W. Lyle (development of applications of boron to electrical engineering) and F. Kroner (copper casting). To them the success of this investigation is largely due.

RESEARCH LABORATORY, GENERAL ELECTRIC CO.
WEST LYNN, MASS.

ACETYLENE SOLVENTS¹

By JOSEPH H. JAMES

The rapidly advancing price of acetone makes it desirable to have commercially available a solvent that can be obtained in any quantity and which shall not advance in price abnormally.

To determine the relative industrial value of various acetylene solvents, a number of laboratory tests and large scale experiments were made. The purpose of this paper is to report the results of this work.

The acetylene used in the laboratory tests was made from commercial carbide in an ordinary "Carbide to water" laboratory generator. It was purified to remove ammonia, sulfur compounds, and phosphorus compounds, by passing through a purifying train consisting of the following: (1) a ten per cent. sulphuric acid solution, (2) a fifteen per cent. hydrochloric acid solution saturated with mercuric chloride, (3) two towers, each containing approximately equal parts of a mixture of bleaching powder and slaked lime, (4) slaked lime, (5) two towers of fused calcium chloride.

In order to get as closely as possible at the true figure for the absorption of acetylene in any of its solvents, it is necessary that the gas be free from impurities and that the solvents be of the highest purity attainable. It has been demonstrated that the solubility drops off rapidly when impurities are present, either in gas or solvent. To get the highest commercial efficiency it will pay to purify the gas and select solvents of highest purity. Care with reference

to the purity of gas and solvent is at present not given the attention in this industry that it deserves.

The detailed method of carrying out this absorption test was as follows:

A carefully measured volume of the solvent (usually 1.5 cc.) was placed in an ordinary five inch side neck test tube, fitted through a two-hole rubber stopper with a glass tube gas inlet, and a thermometer, the bulb of which was immersed in the solvent.

This tube with solvent was immersed in a freezing mixture (ice and salt) and cooled to -18° or -19° C. before starting. The purified gas circulated through a four foot coil immersed in the freezing mixture, thus bringing the gas to the temperature of the solvent.

The acetylene was bubbled through the absorption tube at the rate of about one bubble per second. Since volatile solvents are appreciably vaporized during this process of saturation, the exit gas and vapor in each case was passed through an ordinary potash bulb containing 95 per cent. alcohol; thus the amount of vaporized solvent was determined and proper correction made on the volume of solvent actually used. In twelve minutes the amount of solvent usually taken was completely saturated with the gas at atmospheric pressure; pressure and temperature were always noted. The exit of the absorption tube was then connected to a similar tube two-thirds full of saturated calcium chloride solution which in turn had been saturated with acetylene. The calcium chloride was connected to an ordinary Hempel measuring burette (the liquid in the latter also being a saturated solution of calcium chloride subsequently saturated with acetylene).

The purpose of the calcium chloride was to absorb any solvent vapor that might be carried out in the evolution of the gas, and which would otherwise be measured with the gas giving too high a result. The saturated calcium chloride solution has a very low absorptive capacity for acetylene and it has been proved that it condenses and absorbs completely the vapors of each of the solvents tested. The efficiency of the saturated calcium chloride as an absorbent for the vapor of the various organic liquids used for acetylene solvents was demonstrated by boiling the solvents, and passing the vapor into such an absorbent tube, when the absorption was found to be complete. In several of the experiments noted below, evolved gas from the measuring burette was bubbled back through a "potash" bulb containing 95 per cent. alcohol, but no trace of solvent was found.

Gas evolution begins soon after the absorption tube is removed from the freezing mixture. While the solvent was saturated at -18° C. usually, to guard against the possibility of the solvent not being saturated at the place taken as the starting point, the readings were not noted until the temperature of the solvent had risen to -10° C. The gas evolved from a known volume of the solvent, saturated at -10° C. (since if gas is evolved between -18° and -10° it must be saturated at -10° C.) up to 30° C. is then measured, the figure obtained being recorded in each of the de-

¹ Paper presented at the Fifth Annual Meeting of the American Institute of Chemical Engineers, Detroit, December, 1912.

terminations noted below. The readings are given as actually obtained under the pressure and temperature conditions of the laboratory, and this gas volume is reduced to 0° C. and 760 mm. pressure.

The reason for selecting -10° C. as a point at which the absorptions were determined, was that in commercial practice it is very easy to cool the containers to this temperature. The 30° C. figure was obtained

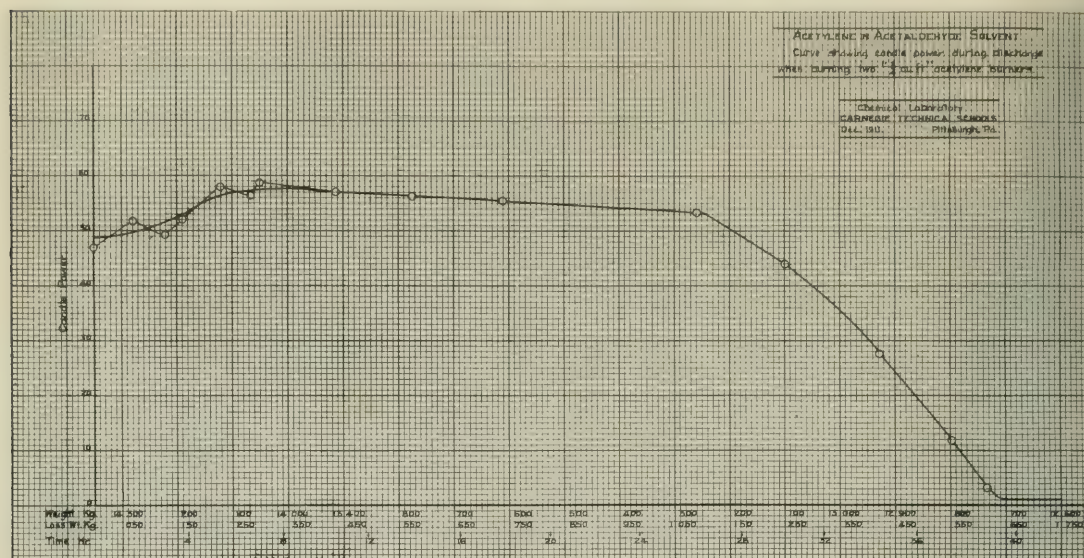


FIG. I—ACETYLENE IN ACETALDEHYDE SOLVENT
Candle power during discharge when burning two $\frac{3}{4}$ cu. ft. acetylene burners

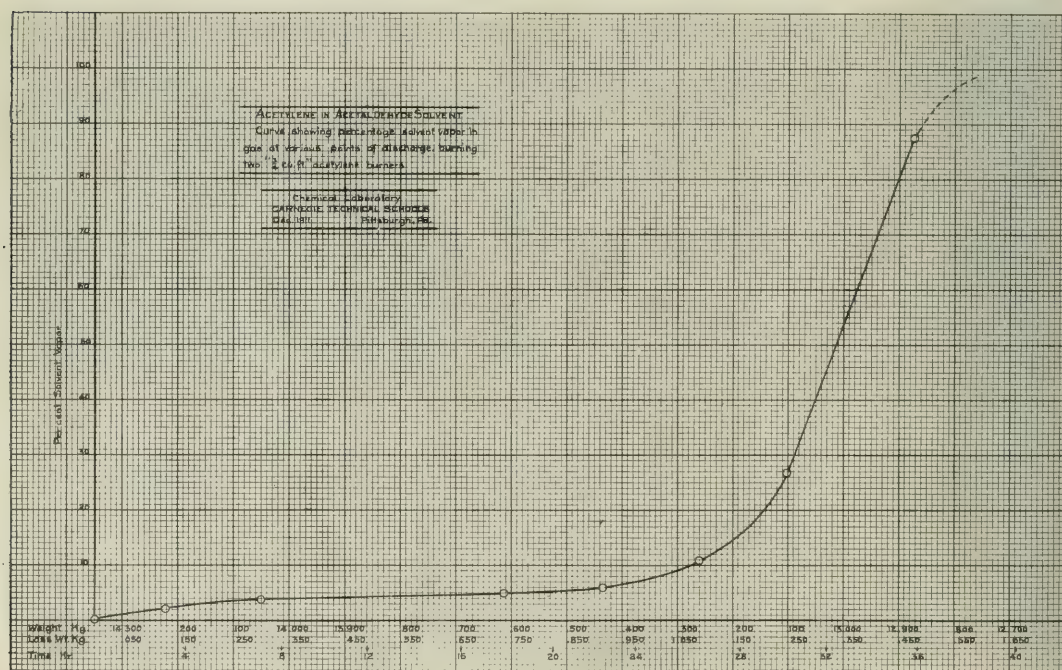


FIG. II—ACETYLENE IN ACETALDEHYDE SOLVENT
Percentage solvent vapor in gas at various points of discharge, burning two $\frac{3}{4}$ cu. ft. acetylene burners

for the reason that with this data the behavior of the solvent could be predicted in practical use, where the gas is rarely evolved at a temperature above 30° C. absorption value of acetone far exceeded that of any solvent studied previously, and some preliminary skirmishing among organic liquids soon led to the view

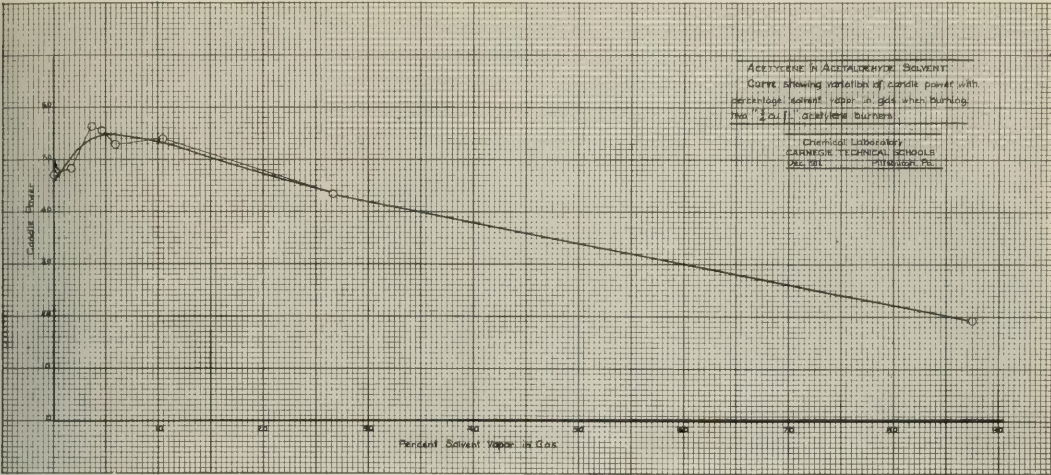


FIG. III—ACETYLENE IN ACETALDEHYDE SOLVENT
Variation of candle power with percentage solvent vapor in gas when burning two "3/4 cu. ft." acetylene burners

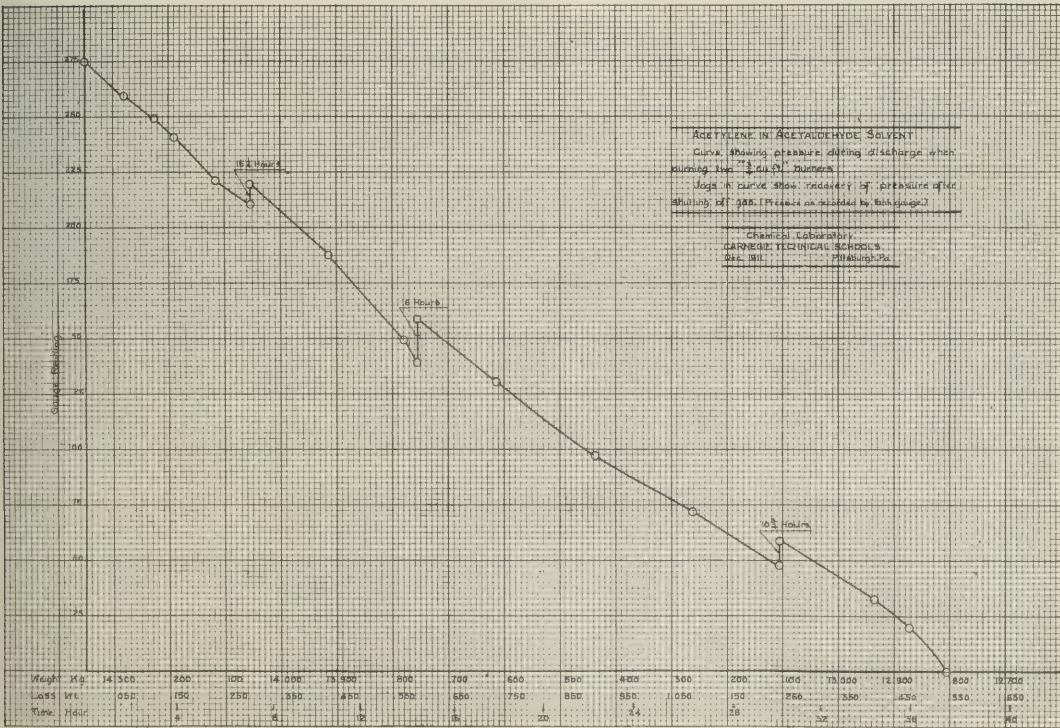


FIG. IV—ACETYLENE IN ACETALDEHYDE SOLVENT
Pressure recorded by tank gauge during discharge, burning two "3/4 cu. ft." burners. Jags in curve show recovery of pressure after shutting off gas

LABORATORY RESULTS

The work of Claude and Hess¹ had shown that the

that the absorption of acetylene in acetone and other carbonyl compounds is partly chemical, in the sense that a chemical reaction or a partial reaction takes

¹ *Compt. rend.*, **124**, 626.

place between the molecules of the absorbent or solvent and molecules of the acetylene. It is well known to organic chemists that the carbonyl group is a very

activity here is quoted in support of von Baecker's "Strain Theory."

With the conception then, that the carbonyl group

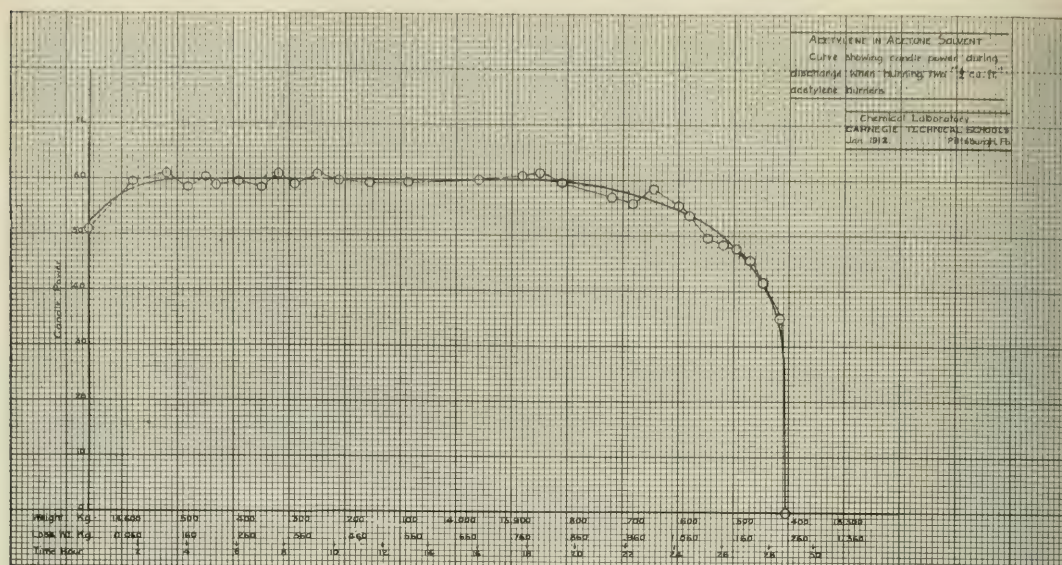


FIG. V—ACETYLENE IN ACETONE SOLVENT
Candle power during discharge when burning two "3/4 cu. ft." acetylene burners

reactive point in the molecule of many carbon compounds, in fact this indicates a condition of strain between the carbon and the oxygen, and the ready re-

in acetone is the reactive point, and that a chemical action of some kind takes place, the solvents noted below were tested. The results establish pretty clearly

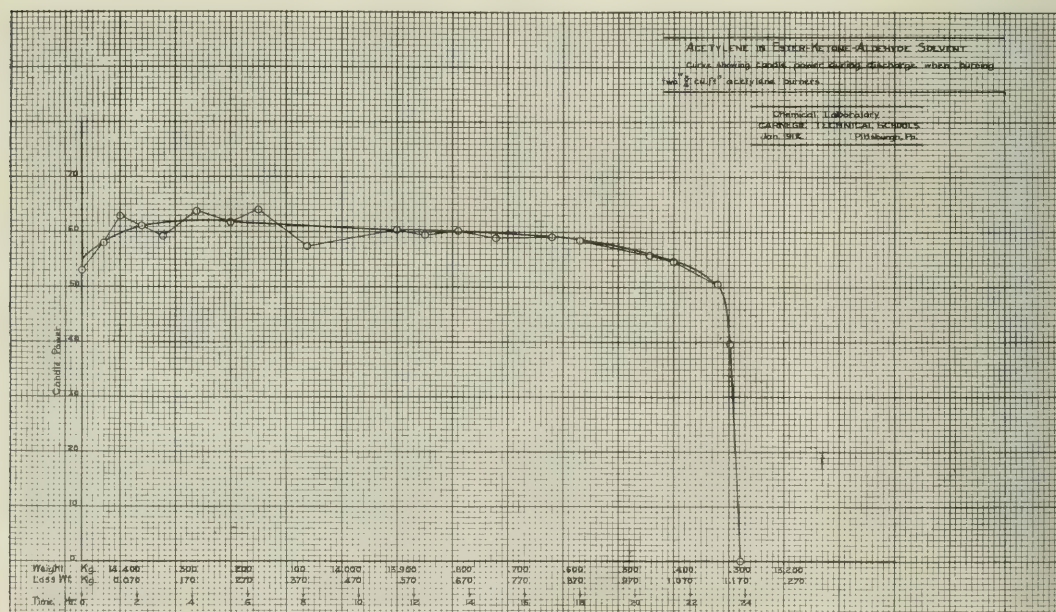


FIG. VI—ACETYLENE IN ESTER-KETONE-ALDEHYDE SOLVENT
Candle power during discharge, burning two "3/4 cu. ft." acetylene burners

that there is a close relation here between the structure and the absorption capacity of a given com-

TABLE I—SOLUBILITY OF ACETYLENE AS DETERMINED BY PREVIOUS OBSERVERS

Solvent	Temperature, Degrees C.	Acetylene dissolved by 1 vol. solvent	Observer
Acetone.....	15	25	Claude & Hess
Acetic acid.....	18	6	Berthelot
Alcohol.....	18	6	Berthelot
Benzoline (gasoline).....	18	4	Berthelot
Chloroform.....	18	4	Berthelot
Paraffin oil.....	0	1	E. Miller
Paraffin oil.....	18	1.5	Berthelot
Carbon bisulphide.....	18	1	Berthelot
Olive oil.....	..	0.48	Fuchs & Schiff
Carbon tetrachloride.....	0	0.25	Nieuwland

TABLE II—PRELIMINARY WORK ON SOLUBILITY OF ACETYLENE
(Figures refer to volume absorbed at $-10^{\circ}\text{C}.$, but volumes are not reduced to standard conditions)

Name	Solvent Boiling point $^{\circ}\text{C}.$	Acetylene dissolved by one vol. solvent at $-10^{\circ}\text{C}.$	Remarks
Ethyl mustard oil.....	131.5	3.2	
Ethylidene cyanhydrin.....	183.0	2.8	
Acetoacetone.....	137 $^{\circ}$	10.2	
Benzophenone, 1 gram dissolved in 23 cc. acetophenone.....			Saturated at $12^{\circ}\text{C}.$, 1.7 volumes absorbed
Methyl propyl ketone.....	102.0	14.8	A crystalline compound of acetylene and acrolein forms during absorption.
Butyric aldehyde.....	74	10.3	
Acrolein.....	52	22.6	
Propionaldehyde.....	48.9	24.2	
Acetaldehyde.....	21	54	
Acetaldehyde, 50 per cent by volume	36	42.2	
Acetone, 50 per cent. by volume			
Acetaldehyde, 50 per cent. by volume	43	40.2	
Ethyl acetate, 50 per cent. by vol.			
Acetaldehyde, 50 per cent. by vol.	32	31.1	
Propionaldehyde, 50 per cent. by vol.			

"Carbonyl theory" is not a complete enough one.

There is also a relation in a given series, usually, between the molecular weight and the absorptive capacity.

The figures obtained are arranged in the preceding tables, the values determined for acetone and certain other organic liquids by previous observers being given for comparison.

SUMMARY OF LABORATORY RESULTS

A study of the figures obtained establishes pretty conclusively that of all the liquids tried, those organic compounds containing the carbonyl group are the best solvents for acetylene. We must exclude the organic acids, as the presence of the free hydroxyl hydrogen seems to work counter to the chemical action upon which the remarkable solubility seems to depend. That the "carbonyl theory" is not satisfactory in every respect is shown by the high figures obtained for methylal and acetal. Their peculiar action seems to require the assumption of quadrivalent oxygen for an adequate explanation.

Further, the figures clearly establish that in a given series the absorption of acetylene is greater the lower the molecular weight of the compound. The above experiments had in view the selection of a solvent that could be used industrially. Since the esters and acetals are out of the question industrially, requiring two and three molecular units per molecule of product, respectively, it was decided to try some larger scale experiments with acetaldehyde, making comparisons with other solvents in commercial use. The amount of acetylene absorbed increases under pressure approximately according to Henry's Law, so the above laboratory results can be used to predict pretty closely what will be absorbed under the pressure used in the acetylene storage industry.

LARGE SCALE EXPERIMENTS

In this series acetaldehyde of between 99 and 99.5

TABLE III—ABSORPTION FIGURES ON ACETYLENE SOLVENTS

CC. ACETYLENE EVOLVED										CORRECTED VOLUME ACETYLENE EVOLVED	AVERAGE ¹ ABSORP- TION
SOLVENT		Boiling point C.	Per cc. solvent					Per cc. of solvent		Per cc. of solvent at -10° C.	
Name			-10° C. to 30° C.	-10° C. to b. pt. of solvent	-10° C. to 30° C.	-10° C. to b. pt. of solvent	Laboratory tempera- ture °C.	Barom. eter read- ing mm.	-10° C. to 30° C.		-10° C. to b. pt. of solvent
Acetaldehyde, C. P.....	20.8	0.76		50.4		66.3	23.0	745		59.9	60.2
		0.81		52.6		65.0	22.0	745		58.8	
		1.44		98.8		68.6	21.5	742		62.1	
Methylal, C. P.....	45.5	1.0	45.2	60.3	45.2	60.3	25.8	735	39.9	53.3	54.3
		1.0	45.4	62.4	45.4	62.4	25.4	735	40.1	55.2	
		1.0	20.4	30.7	20.4	30.7	18.8	742	18.7	28.8	
Acetal, C. P.....	32.3	1.5	70.8	81.5	47.2	54.3	25.6	742	42.1	48.5	48.4
		1.5	69.4	80.9	46.2	53.9	23.5	738	41.4	48.2	
		1.5	46.1	71.1	30.7	47.4	24.5	738	27.4	42.3	
Ethyl formate, C. P.....	54.5	1.5	46.0	70.8	30.6	47.2	24.4	738	27.4	42.0	42.2
		1.5	15.6	30.0	10.4	20.0	23.2	739	9.3	17.9	
		1.5	15.9	28.7	10.6	19.1	23.8	739	9.5	17.1	
Isoamyl formate, C. P.....	123.0	1.5	61.3	82.8	40.8	55.2	22.2	735	36.6	49.5	17.5
		1.5	61.1	91.5	40.7	61.0	21.4	738	36.6	55.0	
		1.5	48.9	72.6	32.6	48.4	18.4	742	29.9	44.4	
Methyl acetate, C. P.....	57.5	1.5	48.4	71.8	32.3	47.9	17.2	742	29.6	44.6	52.5
		1.5	28.8	46.0	19.2	30.6	23.4	739	17.2	27.5	
		1.5	29.0	51.7	19.3	34.5	21.8	738	17.4	31.0	
Ethyl acetate, C. P.....	77.0	1.5	48.9	72.6	32.6	48.4	18.4	742	29.9	44.4	44.5
		1.5	48.4	71.8	32.3	47.9	17.2	742	29.6	44.6	
		1.5	28.8	46.0	19.2	30.6	23.4	739	17.2	27.5	
Isoamyl acetate, C. P.....	139.0	1.5	29.0	51.7	19.3	34.5	21.8	738	17.4	31.0	27.5

¹ Average from preceding column.

pound for acetylene, although the figures obtained for methylal and acetal would indicate that the

per cent. purity was used as the solvent in a regular 6 X 20 inch acetylene storage tank, such as is commonly

used on automobiles, in order to make comparisons with solvents in industrial use as to the amount of gas absorbed, the candle power of the light given on burning the gas from the tank, the loss of solvent, etc. The other solvents were *c. p.* acetone and a complex mixture of organic liquids, which is used as a solvent for acetylene, and which will be referred to in the accompanying curves as ester-ketone-aldehyde solvent since it undoubtedly owes its absorbent power to the presence of bodies belonging to these three groups.

Probably the most important point of comparison is brought out in the curve for each solvent where the candle power at various times of the discharge is shown; a striking difference between the volatile and the non-volatile solvents appears here. With the non-volatile solvents there is little more than an hour's warning before the gas is gone completely, while with the volatile acetaldehyde solvent there is an interval of from four to six hours in length from the first warning and the "going out" of the light. With the acetaldehyde, there is a round black spot in the flame that makes its appearance at about the 35 candle power point of the curve, and the size of this spot increases as the candle power drops, its appearance giving about six hours warning, where two $\frac{1}{2}$ cu. ft. burners are being used.

The loss of solvent, which runs in common practice with the nonvolatile solvents from 4 to 6 ounces for each discharge of the tank, was a fraction over 12 ounces in the acetaldehyde experiment, where the evolution of the gas was pushed to the limit, and would undoubtedly run about 8 ounces in industrial use.

At first glance it appears rather surprising that the drop in candle power with the increase of solvent vapor in the gas is not greater. For example, it is seen from the curve where candle power is plotted against per cent. of solvent vapor in the gas, that when the solvent vapor has increased to 80 per cent. the candle power is still above 20. It has been noted by other observers that diluents lower the candle power of acetylene more rapidly, the lower the flame temperature of the diluent. Since acetylene has a heat of 313.8 cal. per gram molecule, and acetaldehyde has 279.2, we have a satisfactory explanation of the action of the diluent in this case; the calculated temperature of the hottest part of the oxy-acetylene flame is in the neighborhood of 4000° C. and that of the oxy-acetaldehyde flame is above 3400° C.

The aldehyde vapor is a good diluent also for the reason that the volume of air or of oxygen required for its combustion is theoretically exactly the same as that required for acetylene, so that there is scarcely any change in the shape of the flame, as the percentage of aldehyde vapor increases.

These two facts, the high heat of combustion and the equality of the volume of air or of oxygen needed, make for an advantage in the use of acetaldehyde as a solvent for acetylene to be used in welding and cutting operations. In an emergency repair job in a remote locality, in case the gas gives out, the work can be finished by drawing on the volatile solvent for the combustible.

Long observation has shown that the figures attained in industrial practice with the non-volatile solvents noted above, average 37 ounces acetylene in 85 ounces solvent, at a temperature of 70° F. and a pressure of 250 pounds gauge. In this experiment with acetaldehyde as the solvent, 48 ounces of acetylene were absorbed in 82 ounces of solvent, with the gauge standing at 265 when the temperature rose to 70° F. This figure shows that acetaldehyde is a liquid that has a superior absorbent power for acetylene; in fact, the author ventures the statement that this experiment shows an amount of acetylene greater than has ever before been stored in a given volume of solvent.

CONCLUSIONS

I. Acetaldehyde fulfils the industrial requirements for an acetylene solvent.

II. The volatility of acetaldehyde can actually be turned to advantage.

III. Since acetaldehyde can be made in one chemical operation directly from denatured alcohol, we have here a source of supply of an acetylene solvent which will not increase in price, but which will undoubtedly become cheaper as improved methods of agriculture make it possible to produce denatured alcohol cheaper.

Acknowledgment.—I am indebted to my former student assistants, Messrs. E. P. Poste and E. W. Gardner, for their help in taking readings and making records in the above experiments. I wish also to express my thanks to Dr. H. S. Hower, of the Physics Department, Carnegie Institute of Technology, for assistance in taking the candle power readings and for the loan and standardization of the Brodhun Portable Photometer, which was used in the photometric part of the work.

CHEMICAL DEPARTMENT
CARNEGIE INSTITUTE OF TECHNOLOGY
PITTSBURG

TESTS ON THE OPACITY AND HIDING POWER OF PIGMENTS¹

By G. W. THOMPSON

In the discussion of paint problems, certain terms are often used with such different meanings that great confusion has resulted. Thus, the word "covering power" is defined in three or more different senses by Dr. Dudley in his articles in the "*Railroad and Engineering Journal*" running in the issues of 1890 to 1893; and the word "body" has so many different meanings that hardly two persons consider it as referring to the same thing. For this reason, it seemed desirable to Committee D1 of the American Society for Testing Materials that the use of these two terms should be discouraged and they have substituted two simpler terms to cover the more usual uses of these words. These terms and their definitions are as follows:

Hiding Power.—The power of a paint or paint material, as used, to obscure optically a surface painted with it.

¹ Paper presented at the Fifth Annual Meeting of the American Institute of Chemical Engineers, Detroit, December, 1912.

Opacity.—The obstruction to the direct transmission of visible light afforded by any substance, comparison being made with sections of equal thickness. The opacity in the case of pigments should be considered as referable to their opacity in a vehicle under standard conditions.

The distinction between opacity and hiding power should be evident in the study of these definitions. Opacity refers to tests made under standard conditions; and hiding power refers to tests made of paints, etc., as they are used. The distinction becomes clearer when considered with reference to a paint, the opacity of which is measured with a standard thickness of paint, while in the case of the hiding power the thickness of the paint will vary according to the spreading rate at which the paint is applied.

In many laboratories, tests for opacity have been conducted on the assumption that what is known as the strength or tinting strength of a pigment is a measure of its opacity. From numerous tests which we have made, we have come to the conclusion that strength is only an indication of opacity, and that, working on pigments of the same composition, it is not safe to assume that the strength of the pigment is a measure of its opacity. By *strength* or *tinting strength* we mean here:

"The relative power of coloring a given quantity of paint or pigment selected as standard for comparison," which is the definition agreed upon by Committee D of the American Society for Testing Materials. Much heated discussion has appeared in the *Farben-Zeitung* during the last year or more as to whether strength is proportional to opacity. Unfortunately, these discussions are largely academic and not based on practical or accurate tests. As far as the discussions have gone, it would appear that they have not led to any definite conclusion.

Without going into the question of the tinting strength of pigments in this article, we propose to discuss a method which we have developed for the measurement of the opacity of pigments and paints and which will serve, we hope, to some extent, at least, to clear up one phase of this subject.

In developing a method for the determinations of the opacity of pigments, it has been impressed upon us that opacity should never be measured in terms of weight. This has been brought out by Dr. Dudley and by some of the disputants in the *Farben-Zeitung*, but is not as generally recognized as it should be. It seems to us that there can be no question that, in all comparisons of opacity, the relative volume of the pigment should be considered and that a standard of opacity should be based upon a definite volume of the pigment placed in a definite volume of a menstruum. The futility of comparing pigments for opacity by weight is evident where these pigments vary in their specific volumes, as most pigments of different compositions do.

In comparing pigments or paints for opacity, we are compelled to recognize that it is somewhat of a physiological problem. We really have no good means of detecting differences in light except in the

sensations they produce upon the retina of the eye. Photochemical and photoelectrical methods have not, so far, proved satisfactory. This being the case, all photometric work has to be based upon certain standards for comparison. In the case of tests for opacity, however, we have not as great difficulty in this respect as we have in the case of the ordinary photometric measurements. By the use of a single source of light and a suitable photometric bench, the opacity of a substance can be determined with a certain degree of accuracy. Following the method used by Hürter and Driffeld, who worked upon photographic plates, it is possible to construct plates varying in opacity and whose opacity can be determined. It is hardly necessary to describe in detail the method to be followed for this work, and we would refer to the original article by Hürter and Driffeld in the *Journal of the Society of Chemical Industry*, 9, 455 (1890).

There is, however, one difficulty which affects the determination of opacity and the preparation of standard opacity test pieces. In a one-light photometer the light is reflected so as to come from opposite directions and when properly balanced, the light should be equal at zero. By placing the object to be tested in the course of one of these beams of reflected light, the light becomes reduced and the balance of light is found at another point which gives a means of calculating the opacity of the object being tested. Unfortunately, the accuracy of the test depends upon no light being reflected by the object being tested, or that the luminosity or reflecting power of the object being tested shall be determined and applied as a correction to the opacity found.

Hürter and Driffeld worked upon gelatine silver films which, apparently, they assumed had no reflecting power, or that, in their case, the reflecting power could be included by them in the opacity for the practical purposes for which tests were conducted. In the testing of white paints, however, this cannot be assumed, for, as we will show, the amount of light that is reflected is apparently very much in excess of the light that is absorbed during transmission.

According to the best information obtainable, opacity proper follows a logarithmic law known as Bouguer's Law. Nutting, in his recent "Outlines of Applied Optics"—1912, says: "Absorption during transmission follows the logarithmic law in every known case; that is, if a given layer absorbs a certain fraction of transmitted radiation, the next equal layer will absorb the same fraction." Thus, if the first layer absorbs half of the light being transmitted, the next layer will absorb half of the remainder or one-quarter of the light being transmitted; the next layer one-eighth of the light being transmitted, and so on.

To express numerically the opacity of a paint, we should define in some term the light absorbed in transmission for a standard thickness. In a paper read before the International Congress of Applied Chemistry, I suggested that this thickness be 0.1 mm. I find, however, that this thickness was too great for

the proper measuring of opacity and that it would be better to use 0.01 mm. thickness as the unit of thickness in which to express opacity. Of course, any thickness could be used, but it would be better to have a thickness that corresponds to some practical thickness of paint. I, therefore, feel that it would be better to adopt the latter thickness. In expressing the opacity it would seem to me that it should be called the "coefficient," and, having the coefficient, we can calculate the total opacity for any given thickness. We would define, therefore, the coefficient of opacity as the proportion of light, expressed in a decimal fraction of unity, absorbed during transmission through a thickness of 0.01 mm. of paint.



FIG. 1

(Eye-piece is shorter than that used)

We have constructed a piece of apparatus for the purpose of making these tests, which consists, first, of a photometer which will bring two fields of light into juxtaposition so that they can be compared by the eye. This photometer is placed on top of two tubes, the lower ends of which are covered with plano-plano lenses. Below these lenses are two other similar lenses. Below these are two total reflection prisms which direct light from a series of incandescent lamps up through the tubes to the eye and, by adjusting the prisms and the lamps, the light can be made to be equally sent up through the two tubes. The tubes holding the upper plano-plano lenses have micrometer milled wheels on them, so that the distance

between each set of lenses can be controlled and measured. Paint placed between one set of lenses can be compared with a standard paint or with a piece or pieces of paper which have been tested on a photometer bench and the proportion of light they transmit determined. The thickness of the paint can then be varied until the amount of light transmitted matches that transmitted through the standard paint, or the test papers. The thickness of the film of the paint being tested is then read off on the micrometer. Running another test with a different opacity standard of paper or paint, two readings are obtained from which can be calculated the amount of light that is absorbed and the amount of light that has been reflected. Considering opacity as having to do only with the light that is being transmitted, and not to do with the light which is reflected from the surface of the paint, we can figure the coefficient of opacity by the following calculation:

Let a_1 = proportion of light transmitted by test paper No. 1.

a_2 = proportion of light transmitted by test paper No. 2.

$a_1 < a_2$.

b_1 = thickness of paint film transmitting the same amount of light as test paper No. 1.

b_2 = thickness of paint film transmitting the same amount of light as test paper No. 2. Same paint formula is used for b_1 and b_2 .

$b_1 > b_2$.

c = incident light = unity.

x = proportion of incident light reflected which is independent of the thickness of the film except for very thin films.

Then $\frac{a_1}{a_2}$ = proportion of entering light transmitted by

$b_1 - b_2$ thickness of paint, a_2 being the light entering the $b_1 - b_2$ film as it is the light transmitted by the b_2 film.

It is necessary that we give here the development of a formula for the light that passes through any number of units of thickness of paint.

L = the light passing through any number of thickness units.

S = the light absorbed by any thickness unit or units.

a = the light striking the first surface.

A = the ratio $\frac{L}{a}$

B = the ratio $\frac{S}{a} = 1 - A$.

n = the number of units of thickness.

P = the constant opacity of each unit of thickness in the form of a decimal fraction of unity.

Light passing through no unit of thickness:

$$L^0 = a = a$$

Light passing through one unit of thickness:

$$L_1 = a - Pa = a(1 - P)$$

Light passing through two units of thickness:

$$L_2 = (a - Pa) - (a - Pa)P = a(1 - P)^2$$

Light passing through three units of thickness:

$$L_3 = \{(a - Pa) - (a - Pa)P\} - \{(a - Pa) - (a - Pa)P\}P = a(1 - P)^3$$

$$L_n = a(1 - P)^n$$

$$\frac{L_n}{a} = A_n$$

$$\therefore A_n = (1 - P)^n \quad \text{General formula}$$

$$B_n = 1 - A_n = 1 - (1 - P)^n$$

From the formula $A_n = (1 - P)^n$, where A_n is the proportion of entering light transmitted, P is the opacity of unit thickness in terms of decimal of unity and n is the number of units of thickness.

$$a_1 = (1 - P)^{b_1 - b_2}$$

$$a_2 = (1 - P)^{b_1 - b_2}$$

$$P = 1 - \sqrt[b_1 - b_2]{\frac{a_1}{a_2}}$$

From formula $B_n = 1 - (1 - P)^n$ where B_n is the proportion of entering light absorbed:

$$B_{b_2} = 1 - \left[1 - \left(\frac{b_1 - b_2}{1 - \sqrt{\frac{a_1}{a_2}}} \right) \right]^{b_2}$$

$1 - x$ = proportion of incident light entering b_2 film.
 $B_b (1 - x) + x + a_2 = c = 1$

$$\left\{ 1 - \left[1 - \left(\frac{b_1 - b_2}{1 - \sqrt{\frac{a_1}{a_2}}} \right) \right]^{b_2} \right\} (1 - x) + x + a_2 = 1$$

from which

$$x = \frac{1 - a_2 - \left\{ 1 - \left[1 - \left(\frac{b_1 - b_2}{1 - \sqrt{\frac{a_1}{a_2}}} \right) \right]^{b_2} \right\}}{1 - \left[1 - \left(\frac{b_1 - b_2}{1 - \sqrt{\frac{a_1}{a_2}}} \right) \right]^{b_2}}$$

$$x = 1 - \frac{a_2}{\left[1 - \left(\frac{b_1 - b_2}{1 - \sqrt{\frac{a_1}{a_2}}} \right) \right]^{b_2}}$$

This formula looks rather complicated, but, in practice, and by the use of logarithmic tables, the work is more simple than it seems on first inspection.

The apparatus to which I refer reads to the one ten-thousandth of an inch and, preferably, should have been constructed with the millimeter scale. It is a simple matter, however, to make conversions into the mm. scale.

In making these calculations, it is to be observed that, the comparison of the pigments having been made between glass surfaces, the amount of light reflected from the adjacent surfaces of a paint would probably be different from the light reflected from the surface of paint which is adjacent to air. This is a controlling reason why the reflected light should not be considered in calculating the coefficient of opacity.

In testing pigments for their coefficients of opacity, we have followed the plan of mixing these pigments with linseed oil on a standard formula of 25 per cent. by real volume of pigment and 75 per cent. by volume of oil. In some cases, as, for instance, in the case of zinc oxide, this may be too large a volume of pigment, to handle conveniently in the apparatus; but, if trouble is experienced, a different formula can be used, comparing it with another standard pigment on this changed formula.

This apparatus is somewhat new and we have not as many results to report of work done upon it as could be desired, and what we present here is simply for information; and, so that the subject may be more generally studied, we present here some determinations made in this apparatus, working on a number of white pigments. It is not to be supposed that these tests represent average pigments or that the results presented are for the purpose of condemning any of the pigments tested. It is very probable that the pigments upon the market, of the kind described, vary considerably from the figures presented here.

The coefficients of opacity and the light reflected by

the different white pigments, tested on the formula given above, are shown.

The values for P are the coefficients of opacity as defined above. The reflection is the proportion of incident light reflected and is expressed in decimals of unity.

Pigment.	Coefficient of opacity P	Reflection
White lead—Dutch.....	0.0671	0.935
White zinc—American process.....	0.0794	0.956
White zinc—French Pr.....	0.0645	0.964
Lithopone.....	0.0578	0.947
Calcium carbonate.....	0.0136	0.969
Basic lead sulphate.....	0.0813	0.927
China clay.....	0.0190	0.823
Asbestine.....	0.0090	0.859
Calcium sulphate.....	0.0030	0.856
Silica.....	0.0102	0.793
Barytes.....	0.0114	0.856

This work was done in the research laboratory of the National Lead Co., much of it having been accomplished with the assistance of one of my associates, Mr. R. L. Hallett, to whom I tender thanks.

AN APPLICATION OF THE ELECTRIC RESISTANCE FURNACE TO THE DETERMINATION OF OXYGEN IN IRON AND STEEL

By R. H. McMILLEN

Received January 6, 1913

The fact that iron and steel always contain more or less oxygen has long been known, and about thirty years ago, Ledebur¹ called attention to it and gave a method for its determination. It is only recently, however, that the requirements in the manufacture of high-grade steels have become so exacting that the determination of oxygen in steel and other materials has come to be one of the routine determinations required of a steel laboratory.

The Ledebur method, which is well known, consists in heating the sample of iron or steel in nitrogen to remove all moisture without oxidizing it, then reducing the oxides at a red heat by hydrogen and absorbing and weighing the resultant water. Cushman² has shown that the drying of the sample in nitrogen is unnecessary, his results being but slightly higher than those by the original method. When used with electric resistance furnaces, this method is very satisfactory for the determination of oxygen in iron and steel, tungsten,³ and other non-volatile metals. Even this method, however, will fail to show all the oxygen in metals containing oxides of silicon, vanadium, titanium, and other elements whose oxides are not reduced below 950° C.⁴

The following modification of the Ledebur method has been found to give most satisfactory results:

APPARATUS

The apparatus consists of two electric resistance

¹ Sauerstoffbestimmung im schmiedbaren Eisen, *Stahl u. Eisen*, 2, 193.

² "The Determination of Oxygen in Iron and Steel," *THIS JOURNAL*, 3, 372.

³ Tungsten powder often contains a rather large percentage of oxides. Some commercial samples investigated by the writer recently have shown an oxygen content corresponding to 12 per cent. WO_3 . It is probable, however, that the whole of the oxygen is not combined with the tungsten.

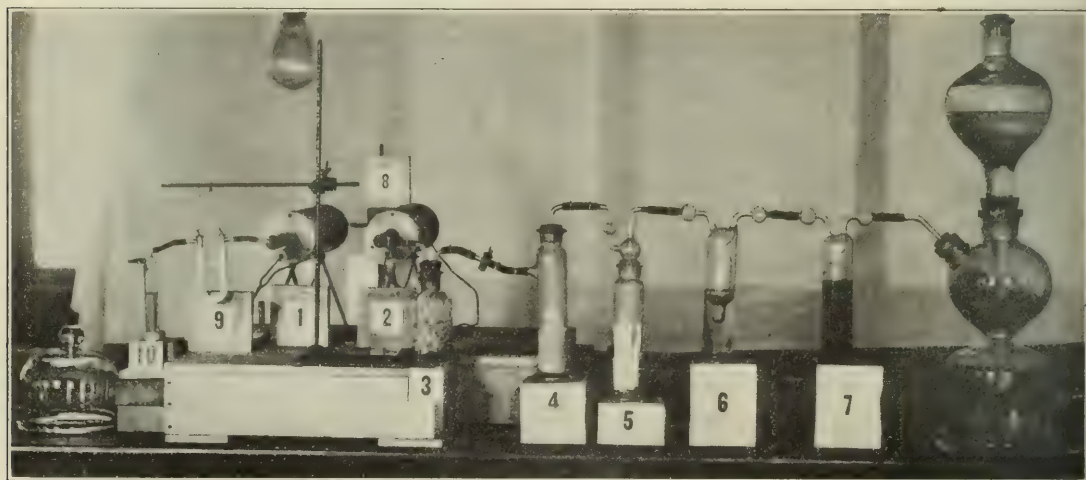
⁴ See "The Determination of Oxygen in Iron and Steel, by Reduction in an Electric Vacuum Furnace," by W. H. Walker and W. A. Patrick, *THIS JOURNAL*, 4, 799.

furnaces, such as are employed in many steel laboratories for combustion carbon determinations and capable of maintaining a temperature of 950°C . They are designated as No. 1 and No. 2 in the illustration. Both furnaces are equipped with heavy-walled, fused quartz tubes $7/8$ inch inside diameter by 24 inches long. The function of furnace No. 1 is to heat the sample under investigation, while that of No. 2 is to heat the hydrogen so that it may combine with any oxygen that may be carried over from the hydrogen generator. Several spirals of platinum gauze are placed in the quartz tube of this furnace. The quartz tubes of these furnaces are connected in the rear by a U tube (not shown in figure) having close-fitting glass stopcocks. This U tube is filled with phosphorus pentoxides opened by small glass beads. The phosphorus pentoxide absorbs any water which may be formed in the tube of furnace No. 2, and insures absolutely dry hydrogen to pass over the sample in furnace No. 1. The front end of the quartz tube in No. 2

so that they be free from rust or foreign oxides. In the case of iron or steel samples both the fine and coarse drillings are rejected, only those between twenty (20) and thirty (30) mesh being used. These are dried for at least one hour over concentrated sulfuric acid before using. Samples of tungsten powders are dried to constant weight in the drying oven at a temperature of 105°C .

PROCEDURE

Twenty-five (25) grams of the prepared drillings are weighed into the dried porcelain boat and placed in the tube of furnace No. 1. Connection is made to the weighed U tube, No. 9, through which, just previous to drying for fifteen (15) minutes and to weighing, hydrogen has been passed for ten (10) minutes. Guard tube No. 10 is connected. Hydrogen is allowed to pass through the whole apparatus at a rapid rate for fifteen (15) minutes. For the first run it is advisable to allow the hydrogen to sweep through the whole apparatus for thirty (30) minutes to insure complete



furnace is connected to the drying and purifying train leading from a hydrogen generator. No. 3 contains small pieces of pumice stone saturated with concentrated sulfuric acid, No. 4 soda lime, No. 5 stick potassium hydrate, No. 6 a 50 per cent. solution of potassium hydrate, No. 7 a 25 per cent. solution of pyrogallol made alkaline with potassium hydrate. Hydrogen is generated in a sixty-four (64) ounce Kipp apparatus by the action of chemically pure hydrochloric acid on pure mossy zinc. The water formed by reduction of oxides in the sample is absorbed in U tube No. 9 of same construction as No. 8, and also filled with phosphorus pentoxide opened with small glass beads. A guard tube, No. 10, is attached to No. 9 and contains concentrated sulfuric acid. A small wash bottle of the Drexel form is used for this purpose. Porcelain boats of sufficient size to hold at least twenty-five (25) grams of the sample are employed.

PREPARATION OF SAMPLE

Great care must be taken in preparing the samples

expulsion of oxygen from the train and tubes. The train and quartz tube of furnace No. 2 can be kept constantly filled with hydrogen by closing the cocks of U tubes No. 8 whenever the flow of hydrogen is interrupted.

The electric current is turned on and continued for one hour after the maximum temperature has been reached. During this time the flow of hydrogen is cut down to about seventy (70) bubbles per minute, this rate being maintained until U tube No. 9 is removed. At the end of the hour the current is turned off and furnaces allowed to cool, accelerating the cooling with a blast of compressed air. When the quartz tubes in the furnaces show no visible redness, the cocks of U tube No. 9 are closed and a pinchcock is inserted over the rubber tube connecting U tube No. 9 to the quartz tube of furnace. In this manner oxygen is kept from the heated tube, thereby avoiding danger of explosion. U tube No. 9 is disconnected and carefully wiped with a soft, dry cloth then desiccated over concentrated sulfuric acid for fifteen min-

utes and finally quickly weighed. Weight of water, after deducting blank, multiplied by 0.8888 divided by 25 equals oxygen.

A blank should be run frequently, adhering to all details as to time of heating furnaces, desiccating U tube, etc. Usually the blank found varies between 0.0015 and 0.0025 gram.

For samples of tungsten powder the same procedure is carried out except that a smaller sample is taken varying from one to ten grams according to the amount of oxygen present.

The following table gives results on several samples in duplicate by the above described procedure:

No.	Oxygen					
	C	Mn	S	P	Si	
1 Crucible steel.....	1.15	0.31	0.018	0.011	0.22	0.039 0.037
2 Crucible steel.....	1.17	0.31	0.015	0.010	0.22	0.035 0.035
3 Crucible steel.....	1.14	0.33	0.016	0.009	0.21	0.044 0.045
4 ¹ Basic open hearth steel....	0.07	0.06	0.019	0.008	0.08	0.113 0.115
5 Basic open hearth steel....	0.08	0.22	0.016	0.008	0.01	0.079 0.072
6 Swedish wrought iron....	0.06	0.17	0.019	0.012	0.02	0.345 0.353
7 Domestic wrought iron....	0.69	trace	0.009	0.007	0.06	0.069 0.076
8 Domestic wrought iron....	0.73	..	0.009	0.007	0.06	0.090 0.089
9 Acid open hearth steel....	0.36	0.69	0.040	0.046	0.03	0.043 0.042
10 Bessemer steel.....	0.46	0.72	0.041	0.095	0.09	0.058 0.060
11 Tungsten powder.....	2.57 2.57
13 Tungsten powder.....	1.37 1.34
14 Tungsten powder.....	0.55 0.56
15 Tungsten powder.....	1.02 1.05

¹ This sample fractured badly in rolling.

Numbers 1, 2 and 3 were three ingots made under as nearly the same conditions as possible. It is not intended that the above table should be typical as to the oxygen content that exists in the different classes of steel. In many samples of crucible steel it is much lower than those cited.

CRESCENT LABORATORY
CRUCIBLE STEEL CO. OF AMERICA
ASPINWALL, PA.

THE VOLUMETRIC DETERMINATION OF MANGANESE IN ROCK, SLAGS, ORES AND SPIEGELS

By F. J. METZGER AND L. E. MARRS
Received November 1, 1912

A new and accurate method for the determination of manganese and its application to the analysis of iron and steel has been published by us in *THIS JOURNAL* (3, 333). The method has since been applied to rock, slags, ores, and spieglers and it is the purpose of this paper to report on these.

Analyzed samples of rocks and of a manganese ore were furnished by W. F. Hillebrand, of the Bureau of Standards. We desire to express our gratitude to Dr. Hillebrand for this material assistance and for the kindly interest he has shown during the progress of our work.

Rock.—Here the manganese content is apt to be very low and for accurate work a portion of from two to five grams should be taken for analysis. Place the weighed portion in a platinum dish; add 5–15 cc. dilute sulfuric acid (1 : 2) and boil; add 5–15 cc. hydrofluoric acid and boil until the rock is completely decomposed. Add 5–10 cc. dilute nitric acid (1 : 1) and 2 or 3 cc. of concentrated sulfuric acid; remove from the flame and add about one gram ammonium persulfate in small portions: when evolution of gas has ceased, evaporate to fumes of sulfur trioxide,

cool, add 50 cc. water, boil and cool. Transfer to a wax beaker, add 5 grams ammonium fluoride and 25 cc. hydrofluoric acid (making a total volume of about 100 cc.) and titrate to a permanent pink color with potassium permanganate solution (approximately *N*/30).

The value of the permanganate in terms of iron multiplied by 0.78682 gives the value in terms of manganese, or by 1.01601 in terms of MnO.

Slag.—Weigh out 0.2–1.0 gram and treat as in rock unless the manganese content is high. If more than about 20–30 mg. of manganese is present in the solution titrated, a brown color will appear toward the end of the titration, but, with a very little experience, as much as 60 mgs. may be titrated with accuracy using a *N*/10 (approx.) permanganate solution. With high percentages of manganese, the titration of an aliquot part of the solution is much more accurate than weighing out exceedingly small amounts. It has been found best to titrate with a volume of about 150 cc. containing about 60 mgs. of manganese when more than 40 per cent. of manganese is to be determined.

If much manganese is present in the solution, oxidized manganese compounds may appear after the addition of the nitric acid to the mixture; the authors have found, on several occasions, a strong permanganate color on taking the mixture to fumes of sulfur trioxide. When this occurs, cool; add 50 cc. water; cool again; add hydrogen peroxide (drop by drop) until the color disappears; boil about ten minutes, cool, and titrate as usual.

Ores.—Pyrolusite: Dissolve 0.5–1.0 gram of the ore in a casserole, using as small a quantity of dilute hydrochloric acid (1 : 1) as possible. Add 15 cc. dilute sulfuric acid (1 : 2) and evaporate to fumes of sulfur trioxide.¹ Cool and add 10 cc. dilute nitric acid (1 : 1) and about 1 gram of ammonium persulfate (have the casserole covered). After evolution of gas has ceased, remove cover and take to fumes of sulfur trioxide. Cool, dilute with water, cool again, transfer to a 250 cc. flask and dilute to the mark. Take an aliquot portion (preferably not less than 0.1 gram of the original ore) and titrate in a volume of about 150 cc., containing 5 grams ammonium fluoride, 10 cc. dilute sulfuric acid (1 : 2) and 25 cc. hydrofluoric acid.

Ores, Slags, etc., Insoluble in Hydrochloric or Nitric Acid.—Proceed as in rock, using peroxide treatment if necessary.

Spiegels (and Ferromanganese).—Weigh out 0.2–1.0 gram and dissolve in 5–10 cc. dilute nitric acid (1 : 1) in a covered casserole; cool slightly and add 1 gram ammonium persulfate; when action has ceased, remove cover, add 15 cc. dilute sulfuric acid (1 : 2) and evaporate almost² to fumes of sulfur trioxide; cool, add 50–100 cc. water;³ heat until ferric salts are

¹ All hydrochloric acid must be removed as titrations made with even small amounts of HCl were decidedly inaccurate.

² Nitric acid up to 2 cc. concentrated acid in a volume of 150 cc. has no effect on the titration.

³ If any oxidized manganese appears here, treat with hydrogen peroxide as described under *Slag*.

dissolved; cool, place in 250 cc. flask, dilute to mark and take aliquot portions for titration (see conditions under Pyrolusite). For all titrations of spiegels use $N/10$ (approx.) permanganate solution.

The subjoined table gives results of analyses of the various products.

Sample	Manganese found ¹	Manganese found by other methods
	Percentage MnO	Percentage MnO
Rock A ²	0.040	0.04
Rock 1	0.246	0.16 ³
Rock 2	0.316	0.28 ³
Rock 3	0.259	0.18 ³
Rock 4	0.278	0.28 ³
Rock 5	0.346	0.22 ³
		Original gravimetric ³
Rock 6	0.23	0.16
Rock 7	0.19	0.10
Rock 8	0.09	0.07
Rock 9	0.30	0.26
Rock 10	0.26	0.20
Rock 11	0.21	0.13
Rock 12	0.11	0.08
Rock 13	0.26	0.22
Iron slag 1	15.91	15.88
		Later colorimetric ⁴
Rock 6	0.23	0.18
Rock 7	0.19	0.13
Rock 8	0.09	0.06
Rock 9	0.30	0.25
Rock 10	0.26	0.19
Rock 11	0.21	0.13
Rock 12	0.11	0.08
Rock 13	0.26	0.23
Iron slag 1	15.91	15.88
		Percentage Mn gravimetric phosphate
Spiegel 1	11.09	11.10
Spiegel 2	21.01	20.99
Spiegel 3	30.55	30.49
Ferromanganese	80.10	80.22
Manganese ore ⁵ dried at 122° C.	57.09	B. of S. certificate
	57.07	High 56.63
	57.11	Low 56.15
		Average 56.36

¹ The results expressed here are the averages of two or more closely agreeing determinations.

² This is a sample of Bureau of Standards argillaceous limestone, analysis by Hillebrand and Walters. See *Jour. Am. Chem. Soc.*, **28**, 223.

³ These results were obtained by W. F. Hillebrand some years ago. Concerning them, Dr. Hillebrand writes: "The manganese was determined with the usual care bestowed on rock analyses, but not in duplicate." And again, "My determinations on these particular rocks were made before I began to determine the small amounts that pass into the filtrates with the lime and magnesia. There was, too, always the possibility, in spite of a basic acetate separation, that a little had not been separated from the Fe and Al."

⁴ "These tests were made with some care, by the color method, correcting for the influence of color due to the iron content of the rocks."—W. F. H.

⁵ Bureau of Standards analyzed "Sample No. 25."

The method has been used successfully in this laboratory for some time. Whereas a little experience is required to accurately determine the end point in titrating large amounts of manganese (40 to 60 mg.), the end point is sharp and distinct and the results are very accurate in determining small amounts of manganese.

The difficulties encountered in determining small amounts of manganese in rock and similar materials are known to analysts and it is believed that the method here described overcomes these difficulties.

It is also believed that the principle involved in the above method may explain some of the discrepancies arising in the determination of ferrous iron in rock.

ANTISEPTIC TESTS OF WOOD PRESERVING OILS¹

By A. L. DEAN AND C. R. DOWNS

The materials commonly employed for impregnating wood for the purpose of preventing its decay fall readily into two classes—soluble salts and hydrocarbon oils. The most widely used member of the first group is zinc chloride, and of the second, coal tar creosote. Ever since the introduction of this last named material by Bethell in 1838 it has been employed in constantly increasing amounts, and today creosoting—properly performed—is regarded as the most effective method of timber preservation.

In recent years the large demand for coal tar creosote and the rather high cost of the treatment with the amounts considered necessary, have led to the use, openly and otherwise, of other materials. Thus the heavy asphaltic petroleum oils have been tried to some extent, notably in the treatments by the Santa Fe railroad where sufficient of the oil has been injected to render the wood well-nigh waterproof. The oil distilled from the tar resulting from the manufacture of carburetted water gas has been used to a considerable extent, but since its value was uncertain it has been regarded as an adulterant or substitute for the oils distilled from coal tar. Water gas tar shows many points of similarity to coal tar, and the creosote oil distilled from it is very like that distilled from coal tar, although it contains neither the phenols nor the nitrogenous bases characteristic of the latter. Inasmuch as large quantities of water gas tar are produced at the gas works in the United States, and the creosote distilled from it might readily be had in substantial amounts, it is important to arrive at a sound estimate of its value as a timber preservative.

The qualities commonly desired in a wood preserving oil are freedom from loss by volatilization, solution or chemical change, and a marked toxicity to wood-rotting fungi and the animals which destroy timber.

In volatility, solubility and chemical inertness water gas tar creosote compares favorably with the oils from coal tar; the relative antiseptic powers of the two classes of oils are less readily determined. The present communication outlines the results of a laboratory study of the antiseptic powers of oils prepared from coal tar and water gas tar, and is designed to assist in arriving at a proper estimate of the place that water gas tar oils should occupy in timber preservation.

The value of water gas tar creosote as a wood preservative has been the subject of some controversy, but as yet the amount of reliable data has not been large. Practical tests on a commercial scale giving the results of the test of time under service conditions have not been carried out. Where the material has been used it has usually been employed in mixture with coal tar creosote, sometimes without the consumer's knowledge. The result has been that in the absence of reliable information consumers have preferred to rely on coal tar creosote of the value of which they were certain.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

Alleman¹ has studied the character of the oils remaining in timbers which, after being treated with coal tar oils, have been many years in service. The results show that the low-boiling oils present in creosote disappear after a number of years of service, and the tar acids or phenols are no longer present. There has been in recent years a growing tendency to regard these high-boiling hydrocarbon oils such as Alleman found remaining in his well preserved timbers as the most valuable constituents of creosote oils.

During 1911, J. M. Weiss² presented two papers to the New York Section of the Society of Chemical Industry, dealing with the antiseptic value of the oils and tars used in timber preservation. These papers showed the relative antiseptic value of coal tar oils and water gas tar oils under the conditions of Weiss' experiments, as well as furnishing some information on the relative values of the different tar oil constituents. These papers furnish the most important experimental evidence of the antiseptic powers of the different oils. The work of Weiss showed that coal tar creosote was many times as toxic to the organisms used in his experiments as the water gas product, and that the lower boiling coal tar oils were distinctly more antiseptic than the heavy high-boiling ones.

Two criticisms may be made of the methods employed by Weiss. The first, and less important, being that the fungi used by him to test the antiseptic powers of the materials experimented on by him were not wood-destroying fungi and their powers of resistance to various agents might not be the same. A much more serious objection to his results depends upon the method employed in preparing the media containing the oils to be tested. These are for the most part insoluble in water and, being heavy, sink rapidly to the bottom of the containing dishes, so that a uniform distribution of the oil is not effected, and the cells of the fungi may not come in contact with it. It is apparent that oils containing water-soluble constituents would partially dissolve and prove more antiseptic than the more insoluble oils. It might readily be that the relatively greater antiseptic power of the lighter coal tar oils was partly due to solubility of the phenols present in them, the toxic power of which is well known. It would seem that a much fairer idea of the antiseptic power of the oils tested could be gained if they were uniformly distributed throughout the culture medium so that the fungus must come in contact with them.

The organism used in the experiments to be described was *Polystictus versicolor* obtained in pure culture from wood decaying through the action of this fungus and bearing masses of its sporophores on the surface. Numerous cultures were kept in the laboratory on small blocks of sterilized *Liriodendron* wood on which it grew readily, and which it reduced to about the specific gravity and strength of pith in the course of a few months. There was no doubt of the purity of the cultures nor of the powerful attack of the fungus

on the wood. This species was used because of the readiness with which it may be isolated in pure cultures which grow vigorously under laboratory conditions, and also because it is one of the most important enemies of structural timber in the United States. Von Schrenck³ says of this species: "Of all the fungi which grow upon the deciduous species of woods after they are cut from the tree, the most widely distributed and in many respects the most destructive is *Polystictus versicolor*. . . . On account of its wide geographical range and its ability to grow on and destroy so many different kinds of wood it should be regarded as the most serious of all the wood-rotting fungi which attack the dead wood of broadleaf trees. It is the fungus which destroys probably 75 per cent. or more of the broadleaf timber used for tie purposes."

Inoculations into the media to be tested could not be conveniently made from cultures growing on wood, and transfers were therefore made to prepared agar from which the fungus could be readily cut and small masses of the mycelium transferred by the use of a small piece of platinum foil set in a glass handle.

The culture media were prepared in the following manner: Ordinary white beans (*Phaseolus vulgaris*) were germinated in a dark place until several inches high. The seedlings were then ground up in a meat chopper and a boiling water extract of them made. Due to the chemical changes characteristic of the process of germination some of the starch of the beans is hydrolyzed to dextrins and sugar, and much of the nitrogen present as the proteins of the seeds appears as soluble cleavage products in the seedlings. One-half of one per cent. of cane sugar and a like quantity of asparagin were added to the germinated bean extract to supply further nourishment. This medium was then stiffened by the addition of 1.5 per cent. of agar agar, and 10 cc. portions of it pipetted hot into 22 mm. test tubes, plugged with cotton and sterilized.

A five-gram portion of each of the creosote oils to be tested was weighed out into a mortar containing an equal weight of powdered gum arabic and the two rubbed well together. Water was then added a little at a time with constant grinding, yielding an emulsion containing as the emulsifying agent a carbohydrate material similar to the agar agar of the medium. The emulsion was diluted with water to 100 cc., making a 5 per cent. emulsion which would not separate even after several months of standing.

Portions of these five per cent. emulsions were measured into the 10 cc. portions of the sterilized agar medium with a pipette graduated to hundredths of a cubic centimeter. As a rule three test tubes of each strength were prepared in order to check the results. The agar was then melted and the tubes well shaken in order thoroughly to mix the emulsion with the medium, and then quickly cooled under cold water in a slanting position. In this way the oil was uniformly distributed throughout the medium in the form of finely divided globules and held permanently in position by the solidification of the agar. .

¹ Gellert Alleman, Circular 98, Forest Service of the U. S. Department of Agriculture, May, 1907.

² J. M. Weiss, *J. Soc. Chem. Ind.*, Feb. 28, 1911, p. 190, and Dec. 15, 1911, p. 1348.

³ Von Schrenck, *Bull.* 149, Bureau of Plant Industry of the U. S. Department of Agriculture, p. 53.

In the first series of tests the oils used were a very good grade of commercial coal tar creosote, a water gas tar creosote made in the laboratory by taking the fraction distilled from 170° to 340° C. from a sample of water gas tar of known origin, and a sample of pressed anthracene oil. The results of the fractional distillation of the two first samples are given in the table below:

TEMPERATURE DEGREES C.	COAL TAR CREOSOTE PER CENT.	WATER GAS TAR CREOSOTE PER CENT.
170	0.2	5.5
170 205	6.3	4.5
205 240	30.7	35.5
240 300	21.3	32.5
300 320	9.1	6.0
320 340	13.5	..

The coal tar oil contained 8 per cent. of tar acids. The anthracene oil was a commercial product, 50 per cent. of which distilled between 250° and 350° C. The solids had been pressed out, leaving it liquid at room temperatures.

The strengths of coal tar creosote tested varied by 0.05 per cent. increments from 0.05 per cent. to 0.35 per cent., and of the other two oils from 0.05 per cent. to 0.75 per cent.

The results of this preliminary series indicated an inhibition point for the fungus with 0.25 per cent. of coal tar creosote, 0.40-0.45 per cent. of the water gas tar creosote, and over 0.75 per cent. for the pressed anthracene oil. In the case of the last named material the growth became progressively weaker, but was not entirely inhibited at the highest concentration tried.

One serious difficulty developed in the tests. In transferring the fungus mycelium to the test tubes it was necessary to cut out a small piece of the agar of the stock culture and it was almost impossible to tell whether the fungus was growing slightly on the creosoted agar or whether all the growth was derived from the small piece of transferred medium. This led to some uncertainty as to the precise point at which growth was inhibited. In the second series, this was remedied by cutting out a small piece of the medium to be inoculated with a sterile platinum foil, laying the cut out piece over to one side, placing the transferred mycelium and agar from the stock culture in the cavity, and then replacing the piece of creosoted medium on top of the transferred material. In this way the mycelium used for inoculation was buried within the mass of material to be tested and if it grew up through it and vegetated at the surface there could be no question that the antiseptic was insufficient to prevent the growth of the fungus. The control cultures were made in the same manner.

The too rapid drying out of the cultures noticed in the first series was prevented in the second by placing them in a large glass walled case with a water-saturated atmosphere.

Since the fungus used in the first series might have had its vitality somewhat impaired by being kept so long in artificial cultures, new samples of wood decaying through the action of the organism were found and fresh, pure cultures prepared and used for inocu-

lating the second series of tests. The following oils were tested:

- A. Coal tar creosote No. 1.
- B. Coal tar creosote No. 2, prepared in the laboratory by taking the fraction distilling from 200° to 350° C. from a sample of coal tar; since there was a considerable separation of naphthalene in this sample on cooling to room temperature, which rendered it impossible to make a satisfactory emulsion, the solids were filtered off.
- C. Water gas tar creosote No. 1.
- D. Water gas tar creosote No. 2, prepared in the laboratory by taking the fraction distilling from water gas tar between 200° and 350° C., yielding a sample somewhat heavier than the No. 1 and comparable in boiling range with coal tar creosote No. 2.
- E. The same sample of pressed anthracene oil used in the first series.
- F. Coal tar creosote No. 1, washed with alkali until free from tar acids and then washed with water.
- G. A portion of F. with the tar bases removed by treatment with sulfuric acid, and washed with water.

An attempt was made to make emulsions with anthracene and naphthalene for antiseptic tests in the manner described above for the oils, but it was found impossible to make satisfactory emulsions. The attempted stock emulsions of these materials containing about 5 per cent. of the hydrocarbons stood for some time in the laboratory and it was noted that a mold growth appeared on the surface. The naphthalene and anthracene had settled to the bottom. This observation would tend to support the statement made by Weiss that these materials were not antiseptic up to 10 per cent. This conclusion seems not to be wholly justified, however, because the mold was not in contact with the hydrocarbons.

The results of the tests in the second series were as follows:

SAMPLE	INHIBITION POINT PER CENT.	
A. Coal tar creosote No. 1.....	Below	0.1
B. Coal tar creosote No. 2.....		0.1
C. Water gas tar creosote No. 1.....		0.4
D. Water gas tar creosote No. 2.....		0.35
E. Pressed anthracene oil.....	Above	0.85
F. Sample A. minus the phenols.....		0.30
G. Sample A. minus the phenols and tar bases.....	Above	0.6

In the case of sample E there was a gradual weakening of the growth from 0.2 per cent. to 0.85 per cent. which was the highest concentration tried, and a similar state of affairs developed in the tests of sample G, the highest strength of which was 0.6 per cent. Of the two, cultures with sample E were slightly the more vigorous.

From these results it is evident that coal tar creosote is a stronger antiseptic than water gas tar creosote, and that water gas tar creosote is distinctly more effective than the liquid oils of the anthracene fraction of coal tar. The greater value of the coal tar oil appears to depend upon the presence of the tar acids and especially upon the tar bases. It is interesting to note that the water gas tar creosote was almost identical in antiseptic power with the coal tar oil with its tar acids removed.

The work of Alleman cited indicated that the oils remaining in wood treated with coal tar creosote are almost free from tar acids after a few years of service, and that under conditions allowing evaporation the lighter hydrocarbons are nearly all lost. Loss of antiseptic power from the disappearance of the tar acids cannot take place with water gas tar oils, since they are free from phenols in the beginning.

Since the amount of creosote injected into wood is commonly 10 pounds per cubic foot or more, it would appear that the difference in antiseptic value between coal tar oils and water gas tar oils is not of great significance, especially in view of the probable disappearance of the tar acids from the wood treated with coal tar creosote.

On the basis of such data as we have it seems justifiable to conclude that the oils distilled from water gas tar have a distinct value as wood preservatives, and that there is no reason why they should not be purchased and used under their own names with no attempt to masquerade as coal tar products.

SHEFFIELD SCIENTIFIC SCHOOL, YALE UNIVERSITY
NEW HAVEN, CONN.

THE OXYGEN ABSORPTION TEST FOR LINSEED OIL¹

By HANS MANNHARDT

This subject has received considerable prominence in this country through a report by a sub-committee on paint oils submitted at the Atlantic City meeting of the American Society of Testing Materials last July. The report covers twelve pages, and to any one taking the time to compare the results of the four experimenters, it must be at once apparent that either the method is not a quantitatively reliable one, or that some essential requirement has been overlooked; their results are to be found in the "1911 Proceedings."

I will quote a few classic and correct results from the standard work on drying oils by Andés, English translation published by Scott, Greenwood & Co., in 1901, where extensive citation is made of Weger's and Lippert's results in the changes in weight which thin films of various oils undergo when exposed to the air on glass plates. Weger's glass surfaces were about 15 square inches in area and on these surfaces he applied weights of oil varying, if possible, only between 25 and 50 milligrams. His results in a condensed form follow:

	Time of drying to maximum change in weight	Per cent. maximum change in weight
Linseed oil, Artists'.....	8 days	17.0
Linseed oil, Artists', heated to 210° C....	5 days	15.5
Linseed oil, English, bottled 5 years.....	3.5 days	19.7
Linseed oil, East Indian seed:		
Raw.....	6 days	17.3
Heated to 150° C.....	6 days	17.0
Cold blown.....	8 days	16.7
Linseed oil, East Indian seed:		
Cold blown, 25 hours }.....	5.5 days	8.2
Hot blown, 25 hours }		
Linseed stand oil.....	18 days	11.1
Litharge boiled linseed oil.....	16 hours	14.6
Linseed oil and 2 per cent. lead manganese resinates (no heat used).....	8.5 hours	17.5
Rosin oil without driers.....	48 days	loss 26.5
Rosin oil (6½ per cent. lead and manganese resinates added at 120° C.) }	6.5 days	gain 25.7
Wood oils, raw, purity not vouched for....	3 to 8 days	+14 to +17
Hemp seed oil, raw.....	4 days	13.6
Poppy seed oil, raw.....	6.5 days	13.4

Looking over the tables in the "1911 Proceedings," I find that the glass area to be covered with a film of drying oil was approximately 35 square inches. The

¹ Read before the Chicago Section of the American Chemical Society, March, 1912. Revised by the author.

several experimenters used weights of oil varying between the following limits:

	Grams
A.....	0.0774 to 0.4011
B.....	0.2877 to 0.9498
C.....	0.2934 to 0.8812
D.....	0.1711 to 2.7318

On the basis of Weger's results they should have used

0.062 to 0.150 gram.

Small wonder that their results were erratic!

You will notice that Weger was successful in drying a film of rosin oil. On page 187 of the "1911 Proceedings" we find statements of three of the experimenters that their films of rosin oil and drier would not set hard. Furthermore, only two of the experimenters found any gaining in weight. The fourth experimenter did not report. Now, W. Pritchard,¹ mentions an XL rosin oil with "rather remarkable drying properties." I also find that thin films of "first run" rosin oil can be caused to set into a non-tacky film by the use of a proper amount of drier, while "second run," "third run" and "fourth run" oils did not appear suitable.

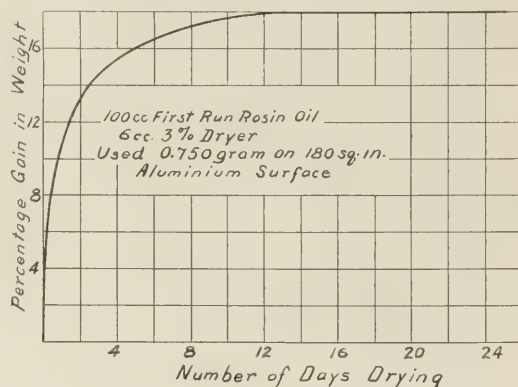


FIG. A

Apparently each redistillation decreases the suitability of the product so that "first run" is at once the cheapest and the most suitable for use in paint vehicles.

That is about all the discussion required by those twelve pages of results in the "1911 Proceedings."

Let us now see what recent literature has to say about the value of the determination of the gain in weight of a film of linseed oil; and in this connection I have selected data bringing out fully the relationship between oxidation by oxygen and by halogen.

Farben-Zeitung, October 1, 1910, page 17, states as follows: "The Hübl iodine values usually vary between 170 and 200 for raw linseed oils, however:—

	Sp. gr.	Acid value	Sapon. value	Unsaponifiable	Hexabromides	Hours drying	Gain in weight	Iodine value
Calcutta.....	0.931	3.1	194.5	1.5	25.2	80	18.0	164.5
La Plata.....	0.932	2.7	193.2	1.7	24.1	85	19.1	161.1
La Plata.....	0.932	2.9	190.4	1.2	22.3	83	18.4	160.2

¹ J. S. C. I., May 15, 1912, p. 420.

This worker apparently used a standardized method for his oxygen absorption test. The last two columns are most vital. I quote these data so fully on account of the low iodine values shown by the three oils, in spite of which fact they appear normal in the gain-in-weight column.

Chem. Revue der Fett u. Harz industrie, 1910, p. 260:

	Per cent. gain in weight	Iodine number.	
Original		153.8	18 hour Hübl method, 98 per cent.
2 hours	5.4	131.6	glacial acetic acid used as sol-
4 hours	10.2	105.0	vent for the films of boiled lin-
6 hours	16.8	73.9	seed oil.
8 hours	17.9	47.3	
10 hours	18.5	26.9	
12 hours	18.6	(a)	

(a) Not completely soluble in the solvent.

This table shows the saturation of the double linkages by oxygen accurately portrayed by the decreasing iodine values.

Jour. Soc. Chem. Industry, Mar. 31, 1911, p. 344, Harry Ingle.

	Specific gravity	Iodine value	Hexabro- mides	
Original oil	0.9315	179.5	35.3	Oil heated in an open enamelled pan at 195° to 200° C.
2 hours	0.9350	175.5	30.7	
4 hours	0.9383	170.0	27.4	
6 hours	0.9418	165.0	26.2	
11 hours	0.9501	154.0	16.0	
15 1/2 hours	0.9583	145.0	10.5	
43 hours	0.9800	121.0	0.9	

This table shows that even the hexabromide test is no criterion of the purity of a linseed oil. The oil, after 43 hours heating, may be said to be approximately in the condition of the boiled oil film of the preceding table about 3 hours old.

Stand Oil.—Sp. gr. $\frac{15.5}{15} = 0.972$ (results, this laboratory).

Bromine addition figure $\frac{51.6}{7.2}$ } McIlhiney method.
"substitution"

Insoluble hexabromides none —Hehner and Mitchell method.

In connection with the method of Dr. McIlhiney, I have devised a convenient form of small funnel which can be constructed by any experimenter and will make the running in of the KI solution much more handy (see Fig. B).

The small cup cut from the bottom of 4 cc. homeopathic vial serves also in weighing out acetone for its determination by the Sy iodoform volumetric method.

Allen, 3rd edition, Vol. II, Part I, p. 66, gives:

Consistency*	Iodine value
Thin	163 to 175
Stout	99.5
Very stout	96.9

*Boiled Linseed oils.

The Stand oil mentioned above was of a molasses consistency. Allen's very stout oil must approach the consistency of a medium printers' varnish.

If we can succeed in establishing the conditions under which a linseed oil film will dry in a normal manner we shall have a quantitative method at our disposal.

Albert H. Hooker had worked out a *practical process for testing drying oils and driers* earlier than 1904 on the basis of Weger's results. The form of apparatus in use by A. H. Hooker consisted of a 3 inch glass crystallizing dish, a small pestle or tamper made by melting the end of a glass rod and upsetting the same, and about 10 grams of finely ground natural silica. One gram of oil or of oil and drier mixture is used in each case and thoroughly incorporated with silica, weighings being taken every 5 minutes at the start until the minimum weight is attained and as often thereafter as may be necessary to obtain an accurate and smooth curve. Often two tests are started on the same day, one at about 8 A.M. and one at about 4 P.M. so as to get complete curves as in the case of the ordinary and double boiled oils.

Lippert calls attention to the importance of detecting the time and amount of the maximum gain in weight, a point not fully appreciated by the above mentioned sub-committee when working with boiled linseed oil. (The practical painter expects to get a boiled oil which will dry in a thin film on glass at 20° C. in less than 24 hours, and if additional driers were added to such an oil the experimenter would have to look for the maximum point before breakfast if the test were started on the day previous.)

The above process of mixing silica and oil is rather tedious and I have expedited the process by using ethyl ether as a vehicle. A tinned-iron can cover about 2 1/2 inches in diameter with a 1/4 inch rim is used as the weighing vessel. One gram of oil is weighed into it and about 10 grams of silica dropped on the oil. By the aid of a spatula and 3 to 5 cubic centimeters of ether the oil and silica are transferred to a large clock glass and then, after thorough mixing, returned to the can cover and the proper weighings made as indicated above.

Liverseege and Elsdon¹ give comparisons of iodine values with percentage gains in drying on powdered

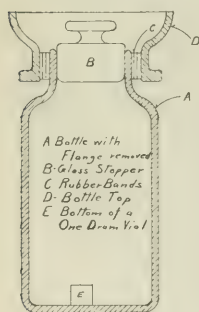


FIG. B

BROMINE ABSORPTION
APPARATUS

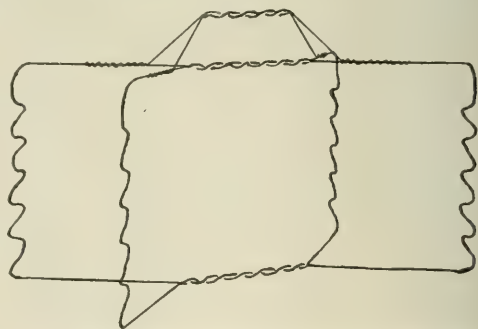


FIG. C—ALUMINUM WIRE PLATE HOLDER FOR HOLDING FIVE ALUMINUM PLATES, EACH 3 IN. X 6 IN., GIVING A TOTAL OF 180 SQ. IN., OF SURFACE

litharge for 8 raw oils and 5 boiled oils. They use a metal container and methylated ether.

¹ *J. Soc. Chem Ind.*, Mar. 15, 1912.

Lippert¹ used aluminum plates for a while but had no good way of cleaning them and abandoned their use in favor of glass apparatus. Since a dried linseed oil film is mildly softened by means of 2 to 3 alcohol to benzole mixture, the aluminum is the proper basis for applying a drying test.

The Standard Varnish Works of Chicago were using a convenient form of apparatus in the latter part of 1904. This apparatus consisted of 5 aluminum plates each 3 inches by 6 inches, and therefore showing a total of 180 square inches of surface. These five plates are held by an aluminum wire frame at intervals of about $\frac{3}{8}$ inch (see Fig. C).

The complete apparatus weighs less than 80 grams and is conveniently weighed on the ordinary analytical balance. The quantity of non-volatile liquid to be applied is kept between 0.500 and 0.700 gram. It is usually applied at the rate of about 2 drops per surface, being uniformly distributed with the tip of a finger. The apparatus is hung under an open shelf to prevent the accumulation of dust. Weighings are made just as in the test on silica.

Results obtained with both forms of apparatus check nicely, as take the case of a bleached oil recently examined:

Specific gravity by Westphal balance $\frac{15.5^{\circ}}{15}$ equals 0.933.

Acidity as oleic acid equals 6.22 per cent.

The writer has used these forms of apparatus successfully for eight and seven years, respectively, and finds the oxygen absorption test to be quite as reliable a test as any other single test.

The addition of a drier hastens the drying but also reduces the actual proportion of drying oil present and in addition decreases the gain in weight of

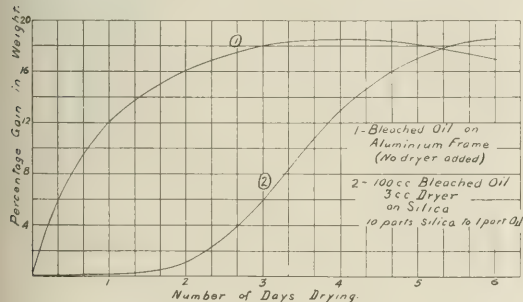


FIG. D

that drying oil which is present.

The addition of a drier is equivalent to a rise in temperature. As oxidation increases the viscosity of linseed oil, I have no doubt that some day specifications for boiled linseed oil will include data on viscosity along with data on the gain in weight.

In conclusion, it may be well to call attention to the fact that tests should be made only:

- a. Along with a control oil of known purity or character.

- b. Using uniform amounts of drier.
- c. Using uniform temperature.
- d. Using definite limited thickness of film.
- e. In an atmosphere of moderate humidity.
- f. With free access of air.
- g. Under the same degree of illumination.

For the convenience of those readers who have not the time to study out the meanings of the technical expressions occurring in the German trade journals, the following translations are given:

<i>Firniss</i> ,	Boiled oil.
<i>Leinoelfirniss</i> ,	Boiled linseed oil.
<i>Lack</i> ,	Varnish.
<i>Lackfarbe</i> ,	Lake Color, Lake.

The author would call attention to the new work, "Die Chemie der Trocknenden Oele," by Wilhelm Fahrion, published by Julius Springer, Berlin, which also makes some references to the results of the work of the linseed oil sub-committee of the American Society for Testing Materials.

1104 OAKDALE AVE.
CHICAGO

A RAPID AND ACCURATE GRAVIMETRIC METHOD FOR DETERMINING MILK-FAT IN EVAPORATED MILK AND MILK POWDERS

By E. P. HARDING AND GUY PARKIN

Received Aug. 12, 1912

The methods in use at the present time for determining milk-fat in evaporated milk and milk powders are inadequate for the use of the manufacturer of these products, either giving too low results or requiring so much time as to make them impracticable. When the percentage of fat in these products becomes a matter of federal state and municipal control, it is necessary that methods be used in their analysis which will record all the fat in order that due justice be given the manufacturer and that they be sufficiently rapid to permit their use in control work.

It is well known that the original Babcock centrifugal method, which is the most rapid of all volumetric methods for determining fat in normal milk, gives by far too low results on the condensed product. Various modifications of this method which have been suggested as giving reliable results were tried out and all found to give too low results, special emphasis having been given to A. E. Leach's modification,¹ and the modification of O. F. Hunziker and G. W. Spitzer.² These methods give not only too low results but also an impure fat and a fat column very difficult to read.

Of all gravimetric methods in use, the Werner-Schmidt method and the Roesse-Gottlieb method³ give the most reliable results. The former method almost invariably gives an impure fat which must be purified by dissolving the dried fat in petroleum ether and filtering. The latter method gives a pure fat but does not remove it all. Results obtained by this method and Hortvet's modification of the same (modified by using a smaller amount of milk in the process) follow later in this paper.

¹ Analyst, **25**, 317.

² Bull. **134**, Purdue Univ. Agric. Experiment Station.

³ Circ. **66**, Dept. of Agr.

¹ Chem. Rev. Fett. Harz Ind., **1897**, 325.

The direct extraction methods like Adams' Paper Coil method and its modifications¹ are impracticable, being too long and giving either too low results or an impure fat.

The writers of this paper, believing the direct extraction methods to be impracticable and the precipitation methods not sufficiently accurate, attempted to solve the problem by indirect extraction methods, *i. e.*, by first dissolving all protein and then extracting the pure fat by some suitable solvent or solvents, as is done in the Werner-Schmidt and Roesse-Gottlieb methods. A modification of a method used by one of the writers and Lillian Nye for determining fat in cereals² was found to give excellent results both in amount and purity of fat.

The principle of the method is the breaking down of the emulsion by dissolving all protein in acetic acid, the solution of the fat in a mixture of alcohol and carbon tetrachloride and its extraction with petroleum ether.

The reagents used are acetic acid, 25 per cent. by volume, redistilled carbon tetrachloride, 95 per cent. ethyl alcohol and petroleum ether with boiling point between 50° and 70° C.

The apparatus used are a mortar and pestle for macerating the can's contents, an evaporating dish of about 50 cc. capacity for weighing out the sample, a 100 cc. flask for making up the 40 per cent. emulsion, a 10 cc. graduated pipette, a 100 cc. Nessler jar fitted with two rubber stoppers, one unperforated and used while centrifuging, the other doubly perforated, bearing blow-off tubes similar to the Werner-Schmidt blow-off tube, a centrifuge, a seven cm. filter paper, funnel and stand, wide-mouthed flasks of 50 to 75 cc. capacity for weighing the fat, a small evaporating dish for holding wash petroleum, a petroleum ether wash bottle, a condenser and drying oven.

In carrying out the process, the can's contents are placed in the mortar and macerated until thoroughly mixed. Forty grams of this mixture are weighed out in the dish, transferred to the 100 cc. flask, the dish well washed with water, the flask filled to the 100 cc. mark with water and then thoroughly shaken to insure a uniform mixture. Four cc. of this mixture are pipetted into the Nessler extraction jar or enough is accurately weighed in the jar to approximate 1.6 grams of the original sample, 8 cc. of acetic acid added and the contents warmed to about 50° C. by cautiously rotating the jar over a low flame or holding it in water of that temperature. When the protein has dissolved, 12.5 cc. of carbon tetrachloride are added and the jar vigorously shaken for two minutes, then 25 cc. of alcohol are added and the whole mixed by thoroughly shaking; 25 cc. of petroleum ether is then added and the jar vigorously shaken for two minutes, then 15 cc. more of the ether added and the shaking continued one minute longer. The jar is then corked and centrifuged for two minutes at the rate of about 70 revolutions per minute. The blow-off tube is then inserted and the ether layer cautiously blown onto the

filter, filtering it into the tared weighing flask. (In blowing off the ether layer, care must be taken that none of the carbon tetrachloride layer is blown off, which may happen if a too close separation of the two layers is attempted. This may be avoided by blowing slowly and observing if any bubbles rise in the tube. If bubbles are seen rising, the blowing is quickly discontinued and they are removed by gently sucking on the blow-off tube.) Five cc. of petroleum ether are then placed in the small evaporating dish and gently drawn into the jar by sucking on the blow-off tube. After a few moments this ether, which has mixed with the thin ether layer in the jar, is blown off and filtered as before. Five cc. of carbon tetrachloride are then added to the contents of the jar, which is thoroughly shaken, then 30 cc. of petroleum ether are added and the jar again thoroughly shaken, then centrifuged for one minute and the ether layer separated and washed once as in the first blow-off. Another addition of 5 cc. carbon tetrachloride and 30 cc. of petroleum ether is made and the separation of the ether layer repeated as in the first blow-off. The filter paper is then well washed with small portions of the petroleum ether, the flask connected with a condenser, the ether distilled off and the flask heated for an hour in an oven at a temperature of 100° C. and then weighed. A fourth blow-off is not necessary as is shown later in the paper.

During the process, while the jar is being prepared for the second and third blow-offs, the weighing flask is connected with the condenser and most of the ether distilled off. This shortens the process some and permits the use of a 50 to 75 cc. flask for weighing the fat.

I. Data obtained on Van Camp's Evaporated Milk by Hunziker's and Spitzer's Modification of Babcock's Method:³

No. 1.	Reading = 2.05×3 = 6.15 per cent. fat.
No. 2.	Reading = 2.01×3 = 6.03 per cent. fat.
No. 3.	Reading = 2.00×3 = 6.00 per cent. fat.
No. 4.	Reading = 2.00×3 = 6.00 per cent. fat.
No. 5.	Reading = 1.90×3 = 5.70 per cent. fat.
No. 7.	Reading = 1.90×3 = 5.70 per cent. fat.
No. 8.	Reading = 2.00×3 = 6.00 per cent. fat.
No. 9.	Reading = 1.90×3 = 5.70 per cent. fat.

These results are not very uniform and are low and in almost every case a charred fat column was obtained which was very difficult to read.

II.—Results obtained with the Harding-Parkin Method: These determinations were made to find out if a fourth blow-off were necessary.

(a) Data obtained by weighing milk sample directly from can without solution. Van Camp's brand of milk was used and each determination represents a different can sample.

No.	1st and 2nd blow-offs		3rd blow-off		4th blow-off	
	Gram	Percent-age	Gram	Percent-age	Gram	Percent-age
1	0.1252	8.25	0.0002	0.01	0.0002	0.01
2	0.1285	8.67	0.0006	0.04	0.0004	0.02
3	0.1366	8.26	0.0004	0.02	0.0003	0.01
4	0.1224	8.12	0.0020	0.10	0.0000	0.00
5	0.1226	8.30	0.0016	0.10	0.0001	0.00
6	0.1456	8.20	0.0020	0.11	0.0002	0.01
7	0.1263	8.25	0.0016	0.10	0.0000	0.00

¹ *Analyst*, 30, 128. *Bull.* 134, Purdue Univ. Agric. Experiment Station.

² *This Journal*, 4, 895.

³ *Bull.* 134, Purdue Univ. Agric. Experiment Station.

(b) Data obtained by using a 40 per cent. emulsion of the milk:

No.	1st and 2nd blow-offs		3rd blow-off		4th blow-off	
	Gram	Percent-age	Gram	Percent-age	Gram	Percent-age
1	0.1295	8.33	0.0005	0.03	0.0003	0.02
2	0.1182	8.34	0.0005	0.03	0.0003	0.02
3	0.1279	8.67			0.0001	0.00

It will be observed that by comparing the data in (a) and (b) that a fourth blow-off is unnecessary and that no error arises in using a 40 per cent. emulsion. There is also less chance of error in sampling in using a 40 per cent. emulsion.

III. (a) A comparison of data obtained on different brands of milk by the Harding-Parkin Method and the Roesse-Gottlieb method as given in *Circ.* 66, Dept. of Agric. These results were determined on samples weighed instead of measured and each determination represents a different can of milk. The starred determinations were run on a 40 per cent. emulsion and the rest on the sample directly from the can:

VAN CAMP'S BRAND									
Harding-Parkin Method					Roesse-Gottlieb Method				
No.	Milk Grams	Fat Gram	Fat Per cent.		Milk Grams	Fat Gram	Fat Per cent.	Diff. Per cent.	
1	1.5100	0.1325	8.77	4.0444	0.3296	8.14	0.63		
2	1.0436	0.0893	8.55		
3	1.5177	0.1252	8.25	4.1270	0.3252	7.87	0.38		
4	1.5069	0.1244	8.22	4.0542	0.3250	8.01	0.12		
5	1.5292	0.1263	8.25		
6	1.4764	0.1242	8.40	3.9948	0.3175	7.96	0.44		
7	1.7786	0.1476	8.31	4.0466	0.3270	8.08	0.23		
8	3.8191	0.1295	8.33	10.2476	0.3282	7.87	0.46		
9	3.4816	0.1182	8.34	10.0283	0.3135	7.70	0.64		
10	4.8942	0.1622	8.21	10.8776	0.3485	7.87	0.34		

(b) The following data were obtained on a 40 per cent. emulsion. The first three determinations were run on the same can sample and 4 cc. were used in the Harding-Parkin method, representing 1.6 grams of the original sample and 10 cc. in the Roesse-Gottlieb method representing 4 grams of the original sample:

ANALYSIS OF A 40 PER CENT. EMULSION									
Harding-Parkin					Roesse-Gottlieb				
Brand	Milk Grams	Fat Gram	Fat Percent-age		Milk Grams	Fat Gram	Fat Percent-age	Diff. Percent-age	
Pet.....	1.60	0.1735	10.84	4	0.4088	10.22	0.62		
.....	1.60	0.1731	10.81	4	0.4143	10.37	0.44		
.....	1.60	0.1730	10.81	4	0.4091	10.22	0.59		
.....	1.60	0.1308	8.16	4	0.3020	7.55	0.61		
.....	1.60	0.1415	8.84	4	0.3281	8.20	0.64		
.....	1.60	0.1368	8.55	4	0.3276	8.19	0.36		
.....	1.60	0.1346	8.41	4	0.3248	8.12	0.29		
.....	1.60	0.1302	8.13	4	0.3080	7.70	0.43		
.....	1.60	0.1368	8.55	4	0.3250	8.12	0.43		
Peerless.....	1.60	0.1254	7.84	4	0.3020	7.55	0.29		
.....	1.60	0.1268	7.92	4	0.3010	7.52	0.40		
.....	1.60	0.1242	7.76	4	0.3016	7.54	0.22		
.....	1.60	0.1245	7.78	4	0.3002	7.50	0.28		

IV. The results in IV were obtained on a 40 per cent. emulsion, the amount of milk used being meas-

ured as in II(b). The method used for comparison was a modification of the Roesse-Gottlieb method by Hortvet, one-half as much sample being used as in the Roesse-Gottlieb method and one additional blow-off being made. Each determination represents a different can sample:

ANALYSES OF A 40 PER CENT. EMULSION									
Harding-Parkin.					Hortvet modified Roesse-Gottlieb				
Brand	Milk Grams	Fat Gram	Fat Per cent.		Milk Grams	Fat Gram	Fat Per cent.	Diff. Per cent.	
Dundee.....	1.6	0.1297	8.11	4	0.1454	7.27	0.84		
Tacco.....	1.6	0.1286	8.04	4	0.1512	7.56	0.48		
".....	1.6	0.1240	7.75	4		
Meadow.....	1.6	0.1261	7.88	4	0.1566	7.83	0.05		
".....	1.6	0.1174	7.34	4	0.1530	7.15	0.19		
Dakonun.....	4	0.1454	7.27		
".....	1.6	0.1200	7.50	4	0.1460	7.30	0.20		
Batavia.....	1.6	0.1395	8.72	4	0.1562	7.81	0.09		
Poppy.....	1.6	0.1603	10.02	4	0.1882	9.41	0.61		
Princess.....	4	0.1540	7.70		
Cornell.....	1.6	0.1363	8.52	4	0.1634	8.17	0.35		
Kahaka.....	1.6	0.1392	8.70	4	0.1610	8.05	0.65		
Van Camp.....	1.6	0.1289	8.06	4	0.1554	7.77	0.29		
Beauty.....	1.6	0.1328	8.30	4	0.1632	8.16	0.14		
University.....	1.6	0.1279	7.99	4	0.1566	7.83	0.16		
Cottage.....	1.6	0.1344	8.40	4	0.1658	8.29	0.11		
Breakfast.....	1.6	0.1350	8.44	4	0.1684	8.42	0.02		
Yours Truly.....	1.6	0.1501	9.38	4	0.1862	9.31	0.07		
Columbian.....	1.6	0.1221	7.63	4	0.1506	7.53	0.10		
Botavia.....	1.6	4		
Every Day.....	1.6	0.1222	7.64	4		
Monarch.....	1.6	0.1291	8.07	4		
Gold Cross.....	1.6	0.1253	7.83	4	0.1544	7.72	0.11		
Peerless.....	1.6	0.1163	7.17	4	0.1428	7.14	0.13		

The determinations in IV were made by Mr. Parkin in Mr. Hortvet's laboratory with the purpose of checking the two methods. The results agree quite closely and, with the exception of three determinations, give an average difference of 0.166 per cent. in favor of the Harding-Parkin method.

To determine whether all the milk fat was removed by the petroleum ether from the admixture of water, alcohol and carbon tetrachloride, a sample of butter fat was purified and dried to constant weight and then put in a solution in the carbon tetrachloride and treated similarly to the milk emulsion.

0.1170 gram of butter fat was taken and 0.1169 gram recovered, giving a recovery of 99.90 per cent.

In conclusion, the writer feels justified in recommending this method for use in the analysis of desiccated milk for the following reasons:

1. It is a short practical method readily adapted to commercial work.
2. It gives a pure fat.
3. It gives a higher per cent. of pure fat than other methods in use.
4. It will give accurate results without a close adherence to the amounts of reagents specified.
5. Justice will be done the desiccated milk manufacturer.

It has been found by a large number of determinations made since the above data were obtained that the use of a centrifuge is not necessary and instead of centrifuging as given in the method after adding the petroleum ether and shaking, the jar is allowed to stand for two minutes, when the separation of the

two layers is complete. In a few cases an emulsion was formed which was immediately broken by adding a few drops of alcohol. The writers therefore make this change in the method, as previously described.

The new method gives good results on chocolate ice cream, where other methods on account of the chocolate fiber have failed to give reliable and accurate results. In applying the method to ice cream, a representative sample was melted, well mixed and 5 grams taken for analysis, 5 cc. of acetic acid, 12 cc. of carbon tetrachloride, 20 cc. of alcohol and 30 cc. of petroleum ether were added and the process carried out as with condensed milk.

The following data were obtained with this method and two other methods on three samples of ice cream, each determination representing a different sample:

Weight taken	ANALYSES OF ICE CREAM		West ¹	Modified Babcock ²
	Harding-Parkin			
	Fat, Gram		Percentages of fat	
5 grams.....	0.6603	13.20	11.75	12.00
5 grams.....	0.6050	12.10	10.00	11.00
5 grams.....	0.8152	16.30	15.00	15.50
5 grams.....	0.6579	13.15	12.00	12.50

¹ West's method is described in the Twelfth Biennial Report of the Minnesota State Dairy and Food Commissioner, p. 56.

² The Modified Babcock Method is described in Food Inspection and Analysis by Leach, 1909 Edition, p. 200, under the heading "Second Method," and a reference is given to Rep. Illinois State Food Commissioner, 1909, p. 80.

The method is at present being tried out on various ice creams, on cheese, cereals, flours and various other products.

Since this paper was written, a modification of Babcock's Volumetric Method by W. Gregory Redmond has appeared in the July, 1912, number of THIS JOURNAL.

UNIVERSITY OF MINNESOTA
MINNEAPOLIS

THE RATE OF THE REACTION OF NITROUS ACID AND UREA IN DILUTE SOLUTIONS

By W. D. BONNER AND E. S. BISHOP

Received Sept. 20, 1912

In Notice of Judgment No. 722, Food and Drugs Act, the following statement¹ is made by Dr. W. S. Haines, a witness for the apellant:

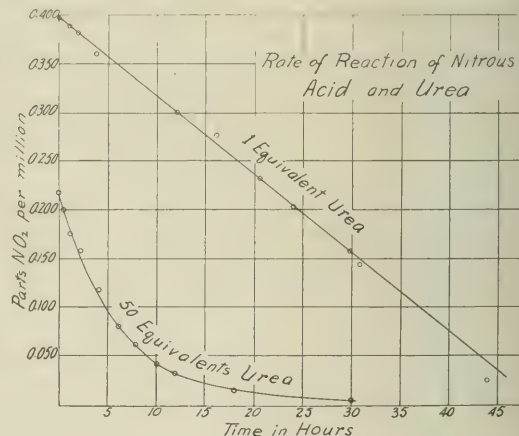
"I believe when nitrites are taken into the body by the mouth that, as they pass into the stomach and the material becomes acid, there are certain substances present in the stomach which cause their decomposition; among others, urea, which is found in the saliva. Urea, it is well known, in the presence of an acid and a nitrite, decomposes the nitrous acid of the nitrite—liberating nitrogen, water and carbonic acid gas. I believe that nitrites, taken into the stomach with our food, are very largely, if not completely, decomposed in the stomach in this way. At body temperature, urea and nitrites react within half an hour."

In the same publication, Dr. S. F. Acree, a witness for the libellant, is reported as saying that he had made experiments to determine whether or not nitrous acid and urea react at body temperature and had found that a solution containing 0.1 part of nitrite nitrogen per million, the average amount assumed

to be present in human saliva, with the equivalent amount of urea and 0.2 per cent. HCl, did not react appreciably in 2 hours, nor was there any appreciable reaction in that time when the concentration of urea was increased 50-fold.¹ He also testified that solutions of the above concentrations do not react appreciably in 17 hours.²

Some experiments performed by one of us during the course of this trial, as well as theoretical considerations, led us to believe the results of this latter witness, and perhaps of both of them, to be in error. They also seemed to indicate that the certainty of the reaction might depend on the purity of the urea used. The following embodies the results of our experiments to settle these two points.

With regard to the second point, we have tried all the samples of urea in the laboratory, including samples of all grades of purity, and have found them, every one, to react with a given sample of nitrous acid, *i. e.*, with a nitrite in acid solution. We have also tried all the nitrites at our disposal, of which there were several samples each of sodium, potassium and



ammonium nitrites, and have found that all of them react readily with urea. The reaction takes place in acid solution only, never in neutral or in alkaline solutions. We do find, however, that sometimes, when working with dilute solutions, one of a pair of duplicates reacts normally, while one does not react. We have not found this behavior in the case of solutions of a concentration as great as 1 part of NO₂ per liter, but when the concentration is 0.1 part per million the occurrence is too frequent to be a mere accident. We have no explanation to offer, but the matter will be investigated further.

As for the other point, *viz.*, the rate of the reaction, reference to the curves will show that both the gentlemen cited above were very decidedly in error.

EXPERIMENTAL

The sodium nitrite and the urea used in these experiments were Kahlbaum's best reagents, and the laboratory distilled water was quite free from ni-

¹ Notice of Judgment, No. 722, page 100.

² Transcript of Record, No. 3543, page 1956.

¹ Notice of Judgment, No. 722, p. 97.

trites. Two methods of preparing the reaction mixture were used. The one was to pipette out separately, from stock solutions of suitable strength, the sodium nitrite and the urea, and to add to the resulting solution sufficient HCl to make the whole 0.3 per cent. HCl. The other was to prepare a stock solution containing both the sodium nitrite and the urea in the desired concentrations, run this into the reaction flasks from a burette, and to add the HCl also from a burette. The latter method was the more satisfactory, since the relation of sodium nitrite to urea was thus always the same, and the actual concentration varied only as the amount of added HCl varied. By adding the acid from a burette this variation could, with reasonable care, be made quite negligible. Before adding the acid the flasks containing the reaction solution were placed in the constant temperature bath and allowed to come to the bath temperature, 37.5°. The bath was electrically heated and controlled and was constant to $\pm 0.1^\circ$. When the reaction solution had come to the temperature of the bath the acid was run in, and the solution then stood in the bath, portions being withdrawn at suitable intervals for the purpose of determining the amount of nitrous acid remaining, until the reaction was complete, or until the solution was exhausted. The nitrous acid was determined by means of the well known Griess-Ilosvay reaction,¹ the color being allowed to fully develop and then compared, in a Schreiner colorimeter, with a standard of known nitrous acid content. The time necessary for the full development of the color we found to be considerably greater than usually stated in the text-books. Sutton says:²

"The solutions are allowed to stand 15 minutes before the pink colors are compared." We find, however, that except in cases where the concentration of NO_2 is greater than 1 part per million the solution should stand a half hour, and when the concentration is very small, 1 or even 2 hours will be needed.

DISCUSSION

That urea and nitrous acid in equivalent quantities should not react to an appreciable extent in 2 hours is perhaps not surprising when one considers the extreme dilution of the solutions, 0.1 part of nitrite nitrogen, or 0.33 part of NO_2 , per million. But when one considers the delicacy of the Griess reaction, detecting easily 1 part of NO_2 per 200 million,³ it seems strange that the progress of the reaction could not be detected in 17 hours. When, however, the concentration of urea was increased to 50 equivalents it would be very strange indeed if the rate of the reaction were then not appreciable. An interesting explanation of how such results as these were got is had by consulting the transcript of record of this case.⁴

There Dr. Acree states that, having mixed the nitrite and the urea solutions and having added the HCl and the Griess reagent, if the nitrous acid and the

urea then react the color of the solution will become lighter, and if the reaction becomes complete the solution will become colorless, "transparent in color." That such is not the case may be seen from the following *a priori* consideration.

Urea and nitrous acid react to produce nitrogen, carbon dioxide and water. Nitrous acid and sulphanilic acid react to produce a diazo compound, which in turn reacts with the α -naphthylamine to produce the dye which is characteristic of the Griess-Ilosvay reaction.¹ Of these two reactions the latter has much the greater rate, *i. e.*, a given amount of nitrous acid will be decomposed by the Griess reagent in much less time than the same amount of nitrous acid would be decomposed by urea. Proof of this is seen in the fact that the one reaction can be used for the detection and estimation of nitrous acid in the presence of urea, that is, while the other reaction is actually in progress. Since the two reactions are simultaneous the situation is analogous to that of two bases competing for less than a sufficient amount of an acid. In this case the "ratio of distribution is equal to the ratio of the respective degrees of dissociation," *i. e.*, the ratio of distribution² is equal to the ratio of the speeds with which the two bases react with one and the same acid. In the present case we have two simultaneous reactions, one of which, when using 50 equivalents of urea, is completed in approximately 24 hours, the other in a half hour or less. When equilibrium is reached, therefore, not more than $1/48$ of the nitrous acid will have reacted with the urea, the rest with the Griess reagent, and no further reaction will occur. Starting with a concentration of nitrous acid of 0.1 part of nitrite nitrogen per million, the difference in color produced by $1/48$ of the nitrous acid reacting with the urea would not be appreciable, the solution could not be distinguished by color from one of the same concentration of nitrous acid and containing no urea. To show that this is actually the case, and that the solution will not become colorless on standing after the Griess reagent has been added, we prepared solutions containing 0.2 part of nitrite nitrogen per million, 1000 parts of urea per million, HCl to make 0.3 per cent. solution, and added the Griess reagent at once. Blanks containing the same concentration of nitrous acid, but no urea or HCl, were prepared, and also duplicates to which the Griess reagent was not added at once, but in which the course of the reaction was followed in the usual manner. These duplicates showed the reaction to be complete in one hour. At the end of 5 hours the solutions containing the Griess reagent were little if any lighter in color than the blanks which contained no urea, and after standing at 37.5° for more than a month the colors were not perceptibly different.

RÉSUMÉ

It has been shown:

(1) That nitrous acid and urea react at an appre-

¹ Sutton, "Volumetric Analysis," 9th Edition, p. 449.

² *Ibid.*, p. 449.

³ See Warrington, *Jour. Chem. Soc.*, **232**, 1881.

⁴ Transcript of Record, No. 3534, page 1956.

¹ The Griess-Ilosvay reagent is sulphanilic acid and α -naphthylamine dissolved in acetic acid. For the course of this reaction see Griess, *Ber. d. chem. Ges.*, **427**, 1879.

² Nernst, "Theoretische Chemie," 5 Auflage, s. 516.

ciable rate even when the initial concentrations are so low as 0.1 part of nitrite nitrogen per million, and urea in equivalent amount.

(2) That once having added the Griess reagent, and thus converted the nitrous acid into the characteristic dye, urea will not then react with the nitrous acid, even though present in great excess.

(3) That nitrous acid and urea, in very dilute solutions, sometimes fail to react, for no apparent reason.

THE GORDON HALL OF CHEMISTRY
SCHOOL OF MINING, KINGSTON, ONTARIO

THE INFLUENCE OF A PRECEDING CROP ON NITRIFICATION IN SOIL

By T. LYTTELTON LYON AND JAMES A. BIZZELL

Received Sept. 11, 1912

While the practices of crop rotations have been fairly well worked out there yet remains much to learn regarding the underlying principles. Most of the effort in experimentation with soils has been to ascertain the effect of certain soil conditions on plant growth or on the solubility of the mineral nutrients in various solvents. The study of the principles of crop rotation will necessitate the investigation of the effect of plant growth on the soil. The fact that a certain plant grows better when preceded by one species of plant than by another is a self-evident indication that plants of different species exert different influences on the soil.

The writers have suggested¹ that certain higher plants have a distinct influence on the process of nitrification in the soil; that this influence varies in intensity with plants of different families, and at different stages in the growth of any one kind of plant. It was found, for instance, that in a soil on which maize was growing the nitrates were sometimes higher at certain periods than in a similar soil on which no plants grew. Timothy (*Phleum pratense*), on the other hand, maintained uniformly a very low nitrate content in the soil throughout the growing period.

The question then arose whether the higher plants exerted any influence on the activities of the nitrifying bacteria after the plants had been removed. To test this it was decided to continue the nitrate determinations a second year in soil that had been planted to several kinds of crops.

Plats that were used for studying the effect of plants on the nitrate content of soils in 1910 were kept bare in 1911 until July 1st. To keep down the weeds the plats were disc harrowed from time to time. Samples of soil were taken from the sections of the plats that were planted and bare in 1910, in order to ascertain the effect of the different crops grown the previous year on the nitrate content of the soil. Soil samples were taken from both the previously planted and unplanted sections of the plats, and the borings were made to a depth of eight inches from the surface, and again from eight to sixteen inches. Table I presents the results, averaged for the entire season, for the four plats planted to the same crop, also the average of the unplanted sections of the same plats during the

growing season of 1910, and consequently shows the nitrate content of the soil in the year during which the test crops were grown:

TABLE I—NITRATES IN PLANTED AND UNPLANTED SECTIONS OF PLATS AVERAGE FOR THE GROWING SEASON

Plat Nos.	Crop	On basis of		
		Nitrates p. p. m. dry soil	nitrates in bare soil 100	Nitrogen in crop Lbs. per acre
3612, 13, 22, 23....	{ Maize	167	123	3.5
	{ None	136	100	
3614, 15, 24, 25....	{ Potatoes	104	96	42.7
	{ None.	108	100	
3616, 17, 26, 27....	{ Oats	90	71	28.7
	{ None	126	100	

The nitrates were highest under the maize, next highest under the potatoes and lowest under the oats. Similar results had been obtained in previous years.

The last column of Table I shows the quantity of nitrogen removed per acre by each crop. The maize crop was a very poor one, which accounts for the small quantity of nitrogen contained in that crop. It is doubtless true that the small maize crop is partially responsible for the high nitrate content of the maize soil, but this high nitrate content has been found in maize soil in previous years when the crop was good. Again, the persistently higher nitrate content of the maize soil, as compared with the bare soil, can be explained only on the assumption that nitrification is much more active where the maize is growing, for certainly more nitrates are being removed from the planted soil.

Nitrates are higher in the potato soil than in the oat soil, although the former crop removed fifty per cent. more nitrogen. The nitrate content of a planted soil is not determined by the total quantity of nitrogen removed by the crop, but by a number of factors, of which one appears to be a direct influence which each species of plant exerts on the activity of the nitrifying organisms.

The year following that in which the results given above were obtained these plats were kept free from vegetation until July 1st and nitrates were determined from time to time. Table II contains a statement of the nitrates of the previously planted and bare sections of these plats on each of the dates when the soils were analyzed:

TABLE II—NITRATES IN SOIL PLANTED THE PREVIOUS YEAR AND SOIL UNPLANTED

Plat Nos.	Crop.	May 1		June 5		June 28	
		First 8 in.	Second 8 in.	First 8 in.	Second 8 in.	First 8 in.	Second 8 in.
3612, 13, 22, 23....	{ Maize	51.5	53.4	77.9	44.6	40.5	34.0
	{ None	48.1	52.3	68.0	44.0	40.3	30.1
3414, 15, 24, 25....	{ Potatoes	31.3	26.0	49.8	26.4	28.6	23.9
	{ None	42.7	43.0	79.7	42.6	35.2	29.4
3616, 17, 26, 27....	{ Oats	22.7	20.7	41.1	33.0	22.1	21.6
	{ None	32.3	39.6	68.4	34.8	33.6	31.9

An examination of this table will show that, except in the case of maize, the nitrates are lower in the soil on which plants grew the previous year than in the soil kept bare at that time. It will also be noticed that the nitrates on this bare soil are in the same order as they were when the plats were planted. That nitrates are highest in the soil previously planted to

¹ Journal of the Franklin Institute, Jan. and Feb., 1911, pp. 1-16, 205-220.

maize, next in that planted to potatoes, and lowest in that planted to oats.

In Table III is given a statement of the nitrates in the planted sections of the plats in terms of the nitrates in the unplanted sections taken as 100. To obtain this the nitrates in both planted ends of the four plats planted to the same crop are averaged and this is divided by the average for the nitrates on the unplanted sections of the corresponding plats. This furnishes the most accurate means of comparison as it removes more effectively than any other method the local variations in the nitrate content of the soil.

TABLE III—RATIO OF NITRATES IN BARE SOIL TO NITRATES IN SOIL OF SAME PLATS PREVIOUSLY PLANTED.

Plat Nos.	Crop.	Surface 8 inches.			Second 8 inches.		
		May	June	June	May	June	June
		1	5	28	1	5	28
3612, 13, 22, 23...	Maize	108	114	100	102	101	112
3614, 15, 24, 25...	Potatoes	73	63	81	60	62	81
3616, 17, 26, 27...	Oats	70	60	66	53	95	68

There is a distinct and characteristic difference in the nitrate content of the soil previously bearing these different plants. While the experiment covers only one season the differences would seem to be too large and well defined to be accidental.

Maize is the only crop following which the nitrates in the planted soil are higher than in the unplanted soil.

These results serve to support the idea already advanced by the writers, that higher plants influence the nitrifying process in soils.

On July 1st the plats used in this experiment were drilled to millet, the entire plat being planted, including the middle section of each plat, which during the preceding year had remained bare. The object in planting the millet was to see how the growth of a crop of these plats would correspond with the nitrate content.

On September 8th careful notes were taken of the growth on each plat and a comparison made not only between different plats but also between the growth of the millet on the previously planted section and the bare section of each plat.

The growth of millet was in each plat markedly better on the sections of the plat that had been in crop the previous year than on the unplanted section. This applied to every crop in the experiment. A comparison of the growth on the planted sections of the plats is given in Table IV, in which the growth of millet on the plats planted to oats is taken as 100 and the growth on the other plats stated on this basis:

TABLE IV—GROWTH OF MILLET ON THE PLATS PLANTED TO DIFFERENT CROPS THE PREVIOUS YEAR

	Soil treat- ment	Plat No.	Growth of mil- let		Plat No.	Growth of mil- let		Average growth of mil- let
			Per cent.			Per cent.		
Maize.....	{ No lime	3612	37	3622	62	49		
	{ Lime	3613	47	3623	71	59		
Potatoes....	{ No lime	3614	60	3624	81	70		
	{ Lime	3615	65	3625	88	76		
Oats.....	{ No lime	3616	100	3626	100	100		
	{ Lime	3617	100	3627	100	100		

It will be seen that the luxuriance of the growth of millet on these plats was inversely proportional to the relative concentration of the nitrates in the soil. For instance, the millet made the best growth on the plats planted to oats and these plats had the lowest nitrate content. The poorest growth of millet was on the maize plats and these had the highest concentration of nitrates.

In Table V the ratio of nitrates to bare soil of the surface eight inches of the several plats on June 28th, which was only a few days before the millet was planted, is compared with the percentage growth of millet on the same plats.

TABLE V—COMPARISON OF NITRATES IN SOIL PLANTED TO CERTAIN CROPS AND THE GROWTH OF MILLET ON THE SAME PLATS

Crop in 1910	Relative nitrate content	Relative growth of millet
Oats.....	59	100
Potatoes.....	67	73
Maize.....	100	54

It would seem from these results that, in this soil, the conditions that favored the growth of millet were unfavorable to the formation of nitrates. That this is not true of other conditions is evident from the fact that the millet grew better on the limed than on the unlimed soil, as shown in Table IV, while the nitrates are also higher in the limed plats, as may be observed in Table VI, which follows:

TABLE VI—NITRATES IN UNPLANTED SECTIONS OF PLATS LIMED AND NOT LIMED.

Plat Nos.	Soil treatment.	Nitrates in soil, p. p. m.			
		May 4	June 5	June 28	Avr.
{ 3612, 22.....	No lime	40.5	61.2	41.8	47.8
{ 3613, 23.....	Lime	54.8	74.9	38.7	56.1
{ 3614, 24.....	No lime	39.9	76.9	34.3	50.3
{ 3615, 25.....	Lime	45.4	82.5	36.0	55.0
{ 3616, 26.....	No lime	28.5	51.7	36.2	38.8
{ 3617, 27.....	Lime	36.2	85.2	40.3	53.9

It is quite evident that although the previous crop influences greatly the nitrate content of this soil, the growth of millet is not increased thereby. Nitrates are not the limiting factor in the growth of millet on this soil.

Lime increases the growth of millet and also the formation of nitrates, but apparently its beneficial action must be due to some cause other than its influence on nitrate formation.

The purpose of this paper is to call attention to the influence of certain kinds of plants on the formation of nitrates in the soil after the crops have been removed. The relation of the nitrate formation to the growth of millet on this soil is a separate problem, probably peculiar to this particular soil, but possibly worth recording in passing. The interesting condition exists that, of the crops used in the experiment, each had a certain and distinct influence on nitrate formation following the removal of the crops, and on the growth of millet also following their removal, but that the effectiveness of the influence is directly opposite. It is not to be expected, however, that this opposite effect would obtain in all soils, since the presence of an abundance of nitrates would, under some circumstances, throw the influence towards a better

growth of the succeeding crop. There is thus presented a problem in crop rotation. If the influence of a certain kind of plant on the formation of nitrates, after its removal, holds for soils, other than the one used in this experiment, something has been learned. That other, and under some conditions, influences more potent than nitrate formation obtain is also indicated by this experiment.

SUMMARY

Plats of land planted to certain crops in 1910 were kept bare of vegetation during the early part of the growing season of 1911. Determinations of nitrates, in the soil of these plats showed a distinct and characteristic relation of the several plants to the nitrate content of the soil in the year following that in which the plants were grown.

Maize was the only crop following which the nitrates in the previously planted soil were higher than in the unplanted soil. Potato soil was the next highest in nitrates, and oat soil contained least nitrates.

Millet planted on these plats July 1st was markedly influenced by previous crops, but the luxuriance of growth was inversely proportional to the nitrate content of the plats.

The beneficial influence of a crop on a succeeding one was not, in this case, to be attributed to the favorable influence exerted on nitrification, but this would doubtless differ with different soils, and if this effect of certain plants on nitrification in the following year should be of general application, the influence of a crop on nitrification may be an important factor in crop rotation.

DEPARTMENT OF SOIL TECHNOLOGY
CORNELL UNIVERSITY
ITHACA, NEW YORK

A COMPARISON OF SOME QUALITATIVE AND QUANTITATIVE METHODS FOR CARBONATES IN SOILS

By E. W. GAITHER

Received Aug. 28, 1912

In connection with certain chemical investigations of soils, which are being conducted in the laboratory of the Chemical Department of this Station, it was found necessary to determine the carbon dioxide existing as carbonates in the soils.

After making a number of determinations by the official method,¹ it was found that there was no correlation between the reaction of the soils with litmus paper or the Veitch qualitative test and the CO₂ obtained by this method.

If it were assumed that the CO₂ was derived from carbonates and it were calculated to CaCO₃, the average amount for acid surface soils would be 3244 pounds CaCO₃ per 2,000,000 pounds of soil and that for acid subsoils would be 1036 pounds per 2,000,000 pounds of soil, which would be a sufficient amount of this material present to render any of these soils alkaline or to indicate that there was a sufficient amount of this compound in all of these soils for all practical purposes. In many cases, where the soil reddened blue litmus, more CO₂ was obtained than from those which turned red litmus blue. These

variations led to the conclusion that this method was unreliable as a measure of soil carbonates.

While considering this point, attention was directed by Mr. J. W. Ames, Chief of the Department, to a method devised by the late F. S. Marr, Carnegie Research Scholar, Rothamsted, England, and published in the *Journal of Agricultural Science*, Vol. III, Part 2, pp. 155-160, for determining CO₂ as carbonates in soils, in which the soil was boiled with very dilute acid under reduced pressure. It is claimed that under these conditions no organic matter is decomposed and that the CO₂ obtained is derived from carbonates only.

Some of Marr's work was repeated and his results were confirmed.

He found that CO₂ was evolved from acid soils even when boiled with distilled water at 100° C. and that the amount was increased upon the addition of a mineral acid, while if boiled at 50° C. under reduced pressure with 2 cc. of conc. HCl per 100 cc. of water, the results were either negative or only a very small amount of CO₂ was evolved. These results were considered to be within the limits of experimental error.

The double titration method of Brown and Escomb with the Amos apparatus¹ was used by Marr, while a slight modification of the same method and an apparatus designed by the writer² was used in this work.³

In checking Marr's work, four soils were chosen, one acid, the other three giving from slight to strong alkaline reactions to litmus and progressive amounts of CO₂ with weak acid under reduced pressure. Comparative results under different treatments follow.

TABLE I—PER CENT. OF CO₂ BY DIFFERENT METHODS OF TREATMENT

Lab. No.	Per cent. CO ₂ when boiled at 100° C. with distilled water 2½ hours	Per cent. CO ₂ when boiled at 50° C. under reduced pressure with distilled water 2½ hours	Per cent. CO ₂ when boiled at 100° C. with 20 cc. of 1-1 HCl and 80 cc. of H ₂ O for 30 mins.	Per cent. CO ₂ when boiled at 50° C. for 30 minutes under reduced pressure with 2 cc. HCl per 100 cc.	Reaction of soil to litmus paper
4715	0.025	0.00	0.190	0.00	Acid
4722	0.010	0.00	0.205	0.01	Sl. alk.
4724	0.015	0.00	0.175	0.03	Alk.
4731	0.265	0.04	4.700	4.62	St. alk.

ABBREVIATIONS USED IN THE PRECEDING AND FOLLOWING TABLES.

A. = acid, Sl. = slightly, St. = strongly, Alk. = alkaline.
Mi. = Miami, V. = Volusia, D. = Dunkirk, Wab. = Wabash and B. or Blk. = Black Gr. = Gravel, Sd. = Sand, Si. = Silt, L. = Loam, and C. = Clay. V. O. W. = Virgin open woodland, V. P. = Virgin pasture, M. = Meadow, P. = Pasture. V. F. R. = Virgin fence row, V. M. G. = Virgin "Maple grove," R. = Road side, C = Cultivated.

From these results it is seen that the soil which reddened blue litmus paper gave no CO₂ when boiled under reduced pressure either with distilled water or with dilute HCl, and that none of the other soils gave CO₂ with distilled water under reduced pressure except 4731, which contained a very large amount, of carbonates, while the acid soil gave more CO₂ when

¹ *Jour. Agr. Sci.*, 1905, 1-322.

² *THIS JOURNAL*, Aug., 1912.

³ The apparatus permits the use of a smaller amount of 4 per cent. NaOH for absorption of CO₂ and makes it convenient to titrate all of the solution rather than an aliquot, thus reducing the analytical error.

TABLE II, PART I—SURFACE SOILS 0-6 INCHES THAT REDDEN BLUE LITMUS PAPER. (SEE FIG. I)

Lab. No		Veitch test	Litmus test	Per cent. CO ₂ by Marr method	Per cent. CO ₂ by official method ¹	Per cent. Humus	Condition ²	Type ¹
4688	1	Acid	Acid	0	0.0242	1.50	C.	Mi. Sd
5081	2	"	"	0	0.0308	0.47	C.	Mi. Si. L.
4687	3	Sl. Alk.	Sl. Acid	0	0.0308	1.53	P.	Waverly Clay
4709	4	Acid	V. Sl. Acid	0	0.0341	0.91	C.	Mi. Sd.
4677	5	Acid	Acid	0	0.0352	1.62	C.	V. Si. L.
4681	6	"	"	0	0.0440	1.18	C.	Mi. C. L.
4680	7	"	Sl. Acid	0	0.0460	1.24	C.	"
4711	8	"	"	0	0.0462	1.47	V. F. R.	Sand
4734	9	Sl. Alk.	"	0	0.0462	1.01	C.	Mi. C. L.
4651	10	Acid	Acid	0	0.0484	1.56	M.	D. Gr. Sd. L.
4652	11	"	"	0	0.0484	1.79	M.	D. Gravel
5668	12	"	"	0	0.0484	3.03	C.	D. Sd. L.
4673	13	Sl. Alk.	Sl. Acid	0	0.0484	1.20	C.	V. Si. L.
4719	14	Acid	Acid	0	0.0506	1.61	C.	Mi. C. L.
4650	15	"	Sl. Acid	0	0.0506	1.52	V. M. G.	D. Sd. Gr. L.
4727	16	Sl. Alk.	Neutral	0	0.0550	1.55	C.	Sandy L.
4655	17	Acid	Acid	0	0.0572	3.54	C.	D. clay
4663	18	"	"	0	0.0572	1.61	C.	Mi. C. L.
4690	19	"	"	0	0.0572	1.13	C.	Mi. Gr. L.
4640	20	Sl. Alk.	"	0	0.0594	1.88	C.	Mi. clay
4671	21	"	Sl. Acid	0	0.0594	1.50	C.	Wab. L.
4684	22	Acid	Acid	0	0.0594	1.57	C.	Mi. C. L.
4642	23	"	"	0	0.0616	C.	"
4643	24	"	"	0	0.0616	C.	"
4661	25	"	"	0	0.0616	C.	"
4704	26	"	Sl. Acid	0	0.0660	2.04	C.	D. Sandy L.
4699	27	"	Acid	0	0.0680	1.21	C.	Blk. Sd. L.
4660	28	"	Sl. Acid	0.0022	0.0682	1.35	V. O. W.	D. clay
4639	29	"	Acid	0	0.0682	2.40	C.	D. Sd. L.
4662	30	"	"	0	0.0682	2.12	M.	Mi. C. L.
4641	31	"	"	0	0.0682	1.74	C.	Sd. L.
5279	32	"	"	0	0.0704	1.25	C.	Mi. C. L.
4675	33	"	Sl. Acid	0	0.0704	1.50	C.	D. Si. L.
4695	34	"	"	0	0.0715	2.31	C.	V. Si. L.
4665	35	Sl. Alk.	Acid	0	0.0726	1.34	C.	Clyde clay
4732	36	"	Sl. Acid	0	0.0748	1.79	M.	Mi. St. L.
4647	37	Acid	Acid	0	0.0770	1.38	M.	Mi. C. L.
4654	38	"	"	0	0.0770	2.09	C.	V. Si. L.
4658	39	Alk.	"	0	0.0770	1.93	C.	D. Gr.
4679	40	Acid	"	0	0.0792	1.62	M.	D. Sd. L.
4733	41	Sl. Alk.	Sl. Acid	0	0.0814	2.49	C.	V. Si. L.
4674	42	Acid	"	0	0.0814	2.17	V. F. R.	Blk. Sd. L.
4715	43	"	"	0	0.0836	2.02	V. O. W.	V. Si. L.
4736	44	"	"	0	0.0902	1.28	V. O. W.	D. clay
4670	45	"	Acid	0	0.0902	1.82	C.	Clay L.
4648	46	"	"	0	0.0946	1.57	C.	D. Gr. L.
4703	47	"	V. Sl. Acid	0	0.0957	2.63	V. O. W.	D. Gr. Sd. L.
4644	48	"	Acid	0	0.0990	2.02	M.	Mi. Si. L.
4657	49	Sl. Alk.	"	0	0.1012	2.40	V. O. W.	V. Si. L.
4721	50	Acid	Sl. Acid	0.0132	0.1034	1.44	R. V. F. R.	D. clay
4683	51	"	Acid	0	0.1078	1.61	V. O. W.	"
5283	52	"	"	0	0.1100	2.21	V. P.	M. C. L.
4685	53	"	"	0	0.1100	3.44	C.	"
4646	54	"	"	0	0.1166	1.71	V. O. W.	Waverly clay
4706	55	"	Sl. Acid	0	0.1188	3.39	V. O. W.	V. Si. L.
4718	56	"	Acid	0.0022	0.1320	3.24	V. O. W.	Clyde clay
4737	57	Alk.	Neutral	0	0.1518	3.15	C.	Wabash loam
								Clyde clay

Average 0.0714 per cent. CO₂ = 3244 pounds CaCO₃ per acre, 7 inches by official method.

TABLE II, PART 2—SUBSOILS 6-36 INCHES THAT REDDEN BLUE LITMUS PAPER. (SEE FIG. II)

Lab. No.		Veitch test	Litmus test	Per cent. CO ₂ by Marr method	Per cent. CO ₂ by official method	Subsoil of surface Soil No.	Condition	Type
4686	1	Acid	Acid	0	0.0022	53	C.	Waverly clay
4710	2	"	Sl. Acid	0	0.0088	4	C.	Sand
4689	3	"	Acid	0	0.0088	1	C.	Sand
4745	4	Sl. Alk.	Sl. Acid	0	0.0110	67	C.	Silt loam
4720	5	Acid	Acid	0	0.0132	14	C.	Clay
4700	6	"	"	0	0.0132	27	C.	D. clay
5280	7	"	"	0	0.0198	32	C.	D. Si. L.
4645	8	"	"	0	0.0220	48	M.	V. Si. L.
4664	9	"	"	0	0.0220	18	C.	Clay loam
4691	10	"	"	0	0.0220	19	C.	Mi. Gr. L.
4672	11	"	"	0	0.0242	21	C.	Wab. loam
4649	12	"	"	0	0.0264	46	C.	D. Gr. Sd. L.
4682	13	"	"	0	0.0264	6	C.	Clay loam
4676	14	"	Neut.	0	0.0319	33	C.	V. Si. L.
4659	15	"	Acid	0	0.0330	39	C.	D. Sd. L.
4666	16	"	"	0	0.0792	35	C.	Mi. Si. L.

Average, 0.0228 per cent. CO₂ = 1036 pounds CaCO₃ per acre, 7 inches by official method.

TABLE II, PART 3.—SURFACE SOILS 0-6 INCHES THAT TURN LITMUS BLUE. (SEE FIG. III)

Lab. No.	Veitch test	Litmus test	Per cent. CO ₂ by		Difference	Per cent. humus	Condition	Type
			Marr method	official method				
4708	58	Acid	0.0011	0.1122	0.1111	2.88	V. O. W.	Clyde clay
4667	59	Alk.	0.0022	0.0726	0.0704	1.19	V. O. W.	Mi. Si. L.
4747	60	Sl. Alk.	0.0033	0.0440	0.0407	0.97	C.	Silt loam
4722	61	Alk.	0.0044	0.0902	0.0858	1.72	C.	Sand
4740	62	Neut.	0.0044	0.0704	0.0660	1.27	River T.	Clay
4746	63	Sl. Alk.	0.0066	0.0462	0.0396	1.43	V. F. R.	Silt L.
4725	64	Alk.	0.0088	0.0968	0.0088	1.80	C.	Sd. C. L.
4701	65	Alk.	0.0110	0.1034	0.0924	3.35	C.	Sand
4724	66	Alk.	0.0132	0.0770	0.0638	1.79	V. S. Y.	Sand
4744	67	Alk.	0.0132	0.0660	0.0528	1.31	C.	Silt loam
5085	68	"	0.0143	0.0528	0.0385	"	C.	Clay loam
4739	69	Sl. Alk.	0.0281	0.1496	0.1215	3.49	V. F. R.	Clay
4730	70	Alk.	0.0484	0.1232	0.0748	1.93	V. B. G.	Clay loam
4741	71	"	0.0506	0.2168	0.1662	6.48	Alluvial	Wabash loam
4751	72	"	0.0506	0.0814	0.0308	0.98	V.	D. clay
4712	73	"	0.0539	0.1210	0.0671	1.96	C.	Clay loam
4749	74	Sl. Alk.	0.0682	0.1210	0.0528	1.13	C.	Silt loam
5083	75	Alk.	0.0792	0.1540	0.0748	1.34	V. O. W.	Silt loam
5281	76	"	0.0946	0.1782	0.0836	1.50	C.	Silt
5087	77	"	0.2530	0.3630	0.1100	3.26	Blk. Swale	Clyde clay
4698	78	Sl. Alk.	0.5632	0.6809	0.1177	1.88	V. F. R.	Clyde clay
4714	79	Alk.	0.5720	0.6600	0.0880	1.23	V. F. R.	D. clay
4743	80	"	1.5220	1.8830	0.3610	6.56	V. Alluv.	Wabash loam

Average difference, 0.0912 per cent. CO₂ = 4144 pounds CaCO₃ per acre, 7 inches by official method.

TABLE II, PART 4.—SUBSOILS 6-36 INCHES THAT TURN LITMUS PAPER BLUE. (SEE FIG. IV)

Lab. No.	Veitch test	Litmus test	Per cent. CO ₂ by		Subsoil of surface	Soil No.	Condition	Type
			Marr method	official method				
4726	1	Sl. Alk.	0	0.0572	0.0572	64	C.	Sd. C. L.
4728	2	"	0	0.0132	0.0132	16	C.	Sd. L.
5082	3	Alk.	0	0.0176	0.0176	2	C.	Mi. Si. L.
5088	4	"	0	0.0286	0.0286	68	C.	Clay L.
4705	5	Sl. Alk.	0.0022	0.0253	0.0231	26	C.	Blk. Sd. L.
4723	6	Alk.	0.0066	0.0462	0.0396	61	C.	Sand
4738	7	Alk.	0.0088	0.1012	0.0924	57	C.	Clyde clay
4656	8	Sl. Alk.	0.0088	0.0396	0.0308	17	C.	D. Clay
4702	9	"	0.0088	0.0242	0.0154	65	C.	Sand
4707	10	"	0.0088	0.0506	0.0418	55	V. O. W.	Clyde clay
4717	11	Alk.	0.0110	0.0682	0.0572	"	C.	Wabash L.
4697	12	"	0.0770	0.1331	0.0562	34	C.	Mi. Blk. C. L.
4742	13	Sl. Alk.	0.3652	0.4048	0.0396	71	Alluv.	Wabash L.
4748	14	Alk.	0.5522	0.6050	0.0528	60	C.	Silt L.
4731	15	"	2.0680	2.1010	0.0330	70	V. B. G.	Clay L.
4713	16	"	2.0900	2.1010	0.0110	73	C.	Clay L.
4750	17	"	2.1030	2.1650	0.0620	74	C.	Silt L.
5086	18	Alk.	7.9090	8.0960	0.1870	77	Blk. Swale	Clyde clay

Average, 0.0477 per cent. CO₂ = 2167 pounds CaCO₃ per acre, 7 inches by official method.

boiled at 100° with distilled water than either 4722 or 4724, and that this was considerably increased for all soils on boiling at 100° with HCl. Sample No. 4731, which contained a very large amount of CO₂, gave nearly the same with acid under both conditions, *viz.*, 0.08 per cent. higher for the strong acid at 100° C., which difference is not far from the average amount obtained from acid soils by boiling at 100° with HCl, as is seen from Table II.

Repeated experiments with other soils gave the same variations as are above shown. Only soils containing large quantities of carbonates gave any CO₂ when boiled with water alone under reduced pressure.

After this preliminary work was done it was decided to make the determination of CO₂ by both methods and compare these results with the litmus paper and Veitch qualitative tests.

For this work 114 samples of soil were used, representing eighteen different types, varying from light sands to heavy clays and from 0.47 per cent. to 6.56 per cent. of humus by the modified Grandeau method; 80 were surface soils, 21 of which were virgin soils from timber lands, fence rows or pastures; 34 were subsoils below the cultivated surface soils.

The litmus paper test was made by moistening the soil with boiled distilled water and making it into a stiff paste, a strip of blue and a strip of red azolitmin¹ paper were placed about an inch apart in a petri dish, covered with a piece of filter paper and the wet soil spread over the filter paper, other strips of red and blue litmus paper were folded and inserted into openings in the soils which were pressed against the folded paper so that when the paper was unfolded it presented a clean surface that had not been in direct contact with the soil. A third set of strips were placed on top of the soil and pressed firmly against it so the contact would be perfect; the cover was then placed on the dish and allowed to remain over night; the comparison was made with a moistened strip of neutral litmus paper. None of the paper was handled with the fingers.

The results were recorded in order of the degree of color change produced in the paper. There was very little difference in degree of color produced by the same soil for any of the methods of applying the paper, and it seemed that one method was as good as the other so long as the soil remained covered and the con-

¹ The best grade of azolitmin paper was used.

tact was allowed to continue for a sufficient time.

The Veitch qualitative test was made by shaking 10 grams of soil with 100 cc. of cold distilled water, free from CO₂, and allowing to settle over night or until sufficiently clear to pipette off 50 cc., to which was added a few drops of phenolphthalein; it was then boiled to about 15 cc. in a 150 cc. Jena beaker and the degree of color recorded, as very slightly alkaline,

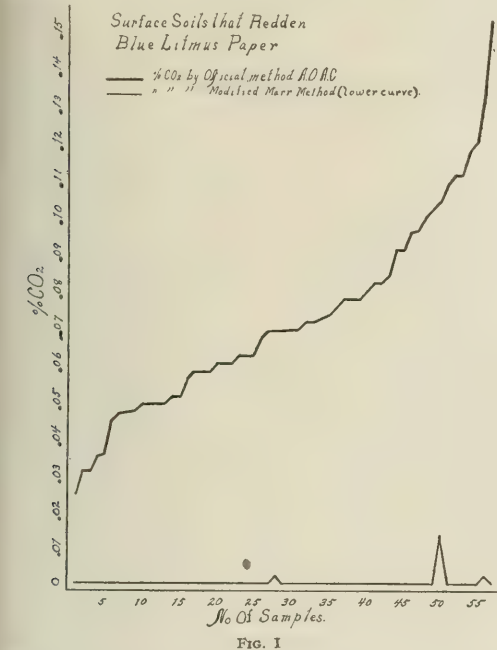


FIG. I

slightly alkaline and alkaline. If no pink color appeared, it was recorded as acid. All these tests were checked by two analysts.

These reactions were tabulated and compared with the CO₂ results obtained by the two methods as found in Table II:

From this table it is seen that there is a very marked agreement between the reaction of these soils and the CO₂ obtained by the Marr method, while there is little or no agreement with the official method.

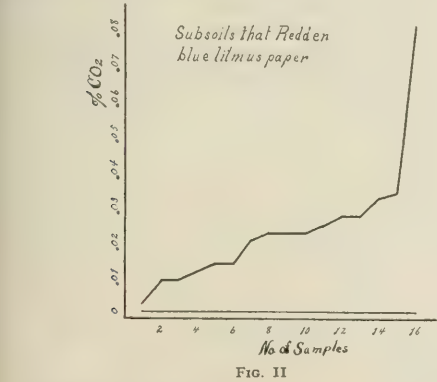


FIG. II

A comparison of the CO₂ by the two methods shows

that for all of these soils there is a wide variation between the two sets of results. In many cases acid soils give more CO₂ by the official method than alkaline soils, especially is this true of surface soils high in organic matter. In the case of subsoils there is a somewhat closer agreement. For soils containing large amounts of carbonates the differences are not very great for such quantities, but are of about the same magnitude as those obtained from soils giving no CO₂ by the Marr method.

TABLE III—LABORATORY NOS. OF SOILS IN WHICH VARIATIONS OCCURRED BETWEEN THE QUALITATIVE TESTS AND CO₂ BY MARR METHOD¹

Depth of sampling Inches	Soils alkaline by Veitch test which gave no CO ₂	Soils alkaline to litmus paper which gave no CO ₂	Soils neutral to litmus paper which gave no CO ₂	Soils acid by Veitch test which gave CO ₂	Soils acid to litmus paper which gave CO ₂	Per cent. of CO ₂ in soils by Marr method
0-6	4718	4718	0.0022
0-6	4721	4721	0.0132
6-36	4726	4726	0
0-6	4727	4727	0
6-36	4728	4728	0
0-6	4732	0
0-6	4733	0
0-6	4734	0
0-6	4737	4737	0
6-36	4745	0
6-36	5082	5082	0
14-24	5088	5088	0
0-6	4640	0
0-6	4657	0
0-6	4658	0
0-6	4660	4660	0.0022
0-6	4665	0
0-6	4671	0
0-6	4673	0
0-6	4687	0
0-6	4708	0.0011

¹ For other data on these samples see Table II.

Table III shows the variations which occurred between the litmus and Veitch tests and the CO₂ from these soils by the Marr method.

Samples 4718-4721 and 4660 were the only soils which were acid to litmus paper that gave any CO₂ at all (these results were checked and four determinations gave the same amount of CO₂). Sample 4718 is a virgin timbered soil overlying an alkaline subsoil containing CaCO₃; 4721 is a virgin soil from a fence row on a roadside and may have been contaminated with CaCO₃ in the road dust; 4660 was a virgin timbered soil; 4708, which was acid by the Veitch test and alkaline to litmus, was a virgin timbered soil, no subsoil being taken. With the exception of these four virgin soils, it is observed that all of the soils, which reddened blue litmus paper, failed to give any CO₂ at all.

Only three soils that react alkaline to litmus paper fail to give CO₂ and these are all subsoils which are only slightly alkaline. This alkalinity, as pointed out by Cameron,¹ may be due to the presence of certain minerals which give alkaline solutions by hydrolysis, independent of the presence of carbonates.

Of the 17 soils that were alkaline by the Veitch test and gave no CO₂, six were alkaline or neutral to litmus paper, the remaining eleven reddened blue lit-

¹ Bureau of Soils, Bull. 30.

mus Some of these gave no alkaline reaction to phenolphthalein when the soil itself was boiled with water and the clear extract tested.

By inspecting Figs. I and II, in which the percentage of CO_2 by the official method is arranged in ascending series, it is readily seen that there is no regularity in the variations of the amount of CO_2 obtained by the two methods. By eliminating the three samples, 4718-4721 and 4660 (to which attention has been directed), the curve representing results obtained by the Marr method becomes a straight line for all soils that redden blue litmus paper, whether surface or subsoils.

For alkaline soils the results by the Marr method

THE METHOD FOR CO_2 IN SOILS

The changes made in the methods used by Marr are in the amount of 4 per cent. NaOH used, the titration of all of the solution instead of an aliquot, and the use of a different apparatus.

Repeated tests using c. p. carbonates and samples of soil justified these changes.

The method as used in this laboratory is as follows:

Put from 2 to 20 grams of soil (depending upon the amount of carbonates present) into any suitable flask or bottle of about 250 cc. capacity that will stand a vacuum of 70 cm. of mercury, add 80 cc. of CO_2 -free distilled water and mix thoroughly, connect to distilling apparatus¹ and start vacuum pump. When

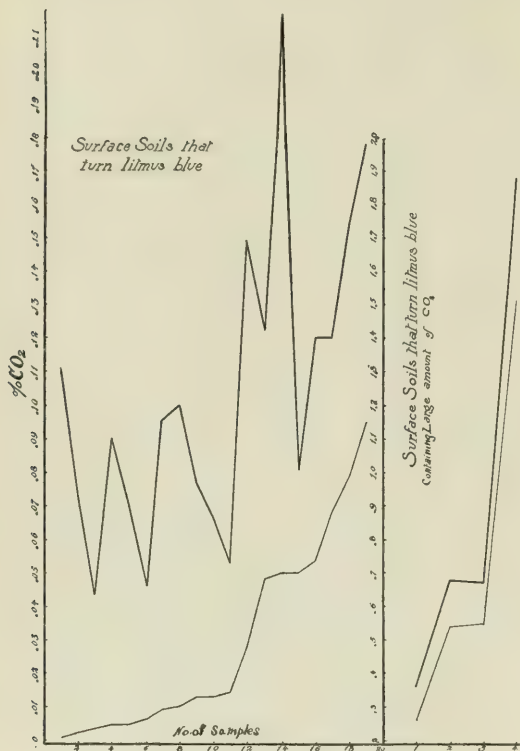


FIG. III

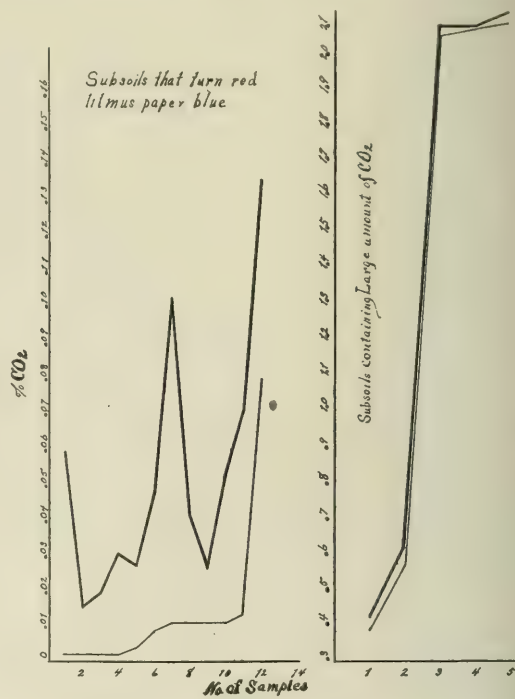


Fig. IV

are arranged in ascending series. Figs. III and IV show that there is still no regularity in the variations of the two methods until the amount of CO_2 approaches 0.3 per cent., from which point the differences are not so noticeable, but are still of about the same magnitude as for soils giving no CO_2 at all.

As a rule, the differences between the two methods are greatest for virgin soils or soils containing large amounts of organic matter.

While no pot or field work has been done on these soils, observations made at the time of sampling and the agricultural history of the sections from which these samples were taken, point to the fact that there is a close agreement between their carbonate content and the productivity of the soils, especially as indicated by the clover yields.

the air has been removed from the apparatus and a vacuum of 65 to 70 cm. is obtained, run in 20 cc. of a solution of HCl (2 cc. HCl , 1.19 sp. gr. to 18 cc. of water) through separatory funnel. Boil for 30 minutes; the CO_2 evolved is absorbed in NaOH made from Na (25 cc. 4 per cent. NaOH and sufficient CO_2 -free water to cover the broken glass rod in the absorbing tower). The bottom of the distilling flask or bottle should be about $\frac{3}{4}$ inches above the gauze protecting it from the free flame. If the liquid is thrown into the condensing tube the flame should be lowered.

Relieve vacuum and draw out the absorbing liquid from the tower into a 400 cc. beaker or Erlenmeyer flask, wash out tower with 250 cc. of CO_2 -free distilled water, add about 1 cc. of phenolphthalein and run in normal HCl until red color begins to fade; finish this titration with $N/20$ HCl . When this end point is reached, add 2 drops of methyl orange solution (1

¹ THIS JOURNAL, 4, 611-612.

gram per 1000) and fill burette with $N/20$ HCl. Take no account of N or $N/20$ acid used in the previous titration. Run in $N/20$ HCl until the lemon color of the alkaline methyl orange just darkens to slight orange,¹ take reading of $N/20$ acid and subtract blank, which should be about 4 cc. 1 cc. $N/20$ HCl = 0.0022 gram CO_2 , 0.0028 gram CaO or 0.005 gram $CaCO_3$.

CONCLUSIONS

The boiling of soils with mineral acids at 100° C. (as pointed out by Cameron, Marr and others) decomposes organic matter and liberates CO_2 which is not present as carbonates and therefore the official method is of no value as a measure of carbonates in soils.

That if soils are boiled under reduced pressure at 50° C. with very dilute mineral acids no organic matter is broken up and the CO_2 evolved is all derived from carbonates.

That the litmus paper test, if properly made, is the best qualitative test we have for the presence or absence of native carbonates in soils from humid regions.

That some soils may give alkaline aqueous solutions, not due to the presence of carbonates but to the hydrolysis of certain minerals which exist in these soils.

That, although the reddening of blue litmus paper by soils may be due to the absorption of the base from the hydrolyzed litmus salt, the presence of native carbonates in a soil may either prevent this selective absorption or cause an interchange of bases to take place.

That if a native carbonate, capable of being decomposed by weak HCl at low temperatures, is present in a soil it is indicated by the bluing of red litmus paper when brought in contact with the moist soil.

That if there are no alkalis or basic materials, in a soil, which are capable of giving alkaline solutions, the absence of such substances will be indicated by the reddening of blue litmus paper.

That if these conclusions are correct, as is strongly indicated by the data already presented, there exists in soils which redden blue litmus paper a condition favorable to the formation of acids or acid salts which would unite with the base absorbed from hydrolyzed litmus and fail to return another base in its stead, thus producing the reddening of the indicator, even though it yields no H ions to a water solution. It is therefore possible that such a soil may be capable of producing a physiological effect similar to that produced by stronger acids which do yield H ions to aqueous solutions.

LABORATORY OF THE CHEMICAL
DEPARTMENT OF THE OHIO
AGR. EXPT. STA.

A CONTRIBUTION TO OUR METHODS OF DETERMINING NITROGEN IN HUMUS

By CHARLES B. LIPMAN AND H. F. PRESLEY

Received Sept. 30, 1912

So far as investigations on the subject have gone to date, nitrogen as nitrates still retains the importance

¹ It will be well for those not familiar with this titration to practice on solutions containing a little Na_2CO_3 . It will be necessary for each analyst to establish and adhere strictly to a constant end point for both indicators.

which must of necessity attach to an essential and very elusive element of plant food. While some plants may prefer to take up nitrogen as ammonia there can be but little question as yet that most plants prefer the nitrate, and we have further evidence that in the absence of such nitrate material the enforced absorption of ammonia by plants is apt to result in certain manifestations of disease due to the disturbance of their physiological mechanism. This, therefore, together with the fact which Hilgard has pointed out,² that *unhumified* organic matter, in his definition of the term, will not nitrify, would appear to invest the humus determination in soils by some method similar to that of Grandeau³ with primary importance in the chemical analysis of soils. Equal importance will, of course, attach to the nitrogen determination in humus since from what has been said above it is that, and not the total soil nitrogen, which may be depended upon to yield through nitrification an available supply of nitrogen to plants.

The general acceptance of the views above given has led to the prosecution of extensive studies looking toward the perfection of the method for determining humus in soils and the reader is referred for a discussion thereof to the recent work of Alway³ and his associates and to that of Kelley and McGeorge.⁴ But while much work has been done on the method of determining humus, but little or no systematic work has been done on the determination of nitrogen in the humus since it has always been assumed that the latest modifications of the Kjeldahl or Gunning method were as reliable for determining nitrogen in the humus as they were for determining that element in other substances. To obtain a more reliable and uniform method for this determination we have carried out a series of investigations in which some of the best known methods for the determination of nitrogen in humus were compared and the results of which we describe below.

HUMUS EMPLOYED IN THE EXPERIMENTS

In order to experiment with widely different kinds of humus we extracted soils of low, good, and very high humus content in accordance with the method outlined in *Circ. 6*, of the California Agricultural Experiment Station. The soils employed for this purpose were as follows:

No. 1. Light sandy soil from walnut orchard, Anaheim, California. Humus content 0.55 per cent.

No. 2. Silty clay loam derived from the State of Washington. Humus content 8.89 per cent.

No. 3. Tule soil from island in the Sacramento River. Nearly all organic matter. Humus content 28.7 per cent.

EXPERIMENTS ON THE DETERMINATION OF NITROGEN IN VARIOUS HUMUS SOLUTIONS

Portions of fifty cubic centimeters of humus extract were boiled with one gram of magnesium oxide in 500 cc. Jena Kjeldahl digestion flasks until no more ammonia was given off as indicated by a test with

¹ "Soils," Macmillan & Co., 1910, p. 359.

² *Circ. 6*, California Agr. Expt. Station.

³ *Bull. 115*, Nebraska Agr. Expt. Station.

⁴ *Bull. 33*, Hawaii Agr. Expt. Station.

litmus paper. The residue was then treated for the digestion of the nitrogen by the different methods whose relative efficiency was to be tested. All the methods given are so well known as to need no further description here. The last method, which was first suggested by Hibbard, as a result of some of his investigations on fertilizers, deserves brief description here, however, since it was published only recently¹ and because it has given by far the best results in our hands. The method of digestion as proposed by Hibbard consists in treating the substances to be analyzed with 30 cc. of concentrated H₂SO₄ until fumes of SO₃ begin to come off. There is then

I. The Hibbard method of digestion gives the highest amounts of nitrogen in all cases except one (see Soil No. 3), thus showing a more thorough digestion.

II. The duplicate and triplicate determinations show the best agreement when the Hibbard method is employed.

III. The digestion is carried out most rapidly by the Hibbard method and, particularly, much more rapidly than by the salicylic acid method which, in other respects, comes the nearest to the Hibbard method in yielding satisfactory results.

IV. In all the methods employed, considerable trouble with bumping was experienced except with

COMPARISON OF NITROGEN DETERMINATIONS BY DIFFERENT METHODS

Method of N determination employed	Soil No. 1			Soil No. 2			Soil No. 3		
	Time necessary to clear solution Minutes.	Nitrogen found Mg.	Per cent. nitrogen in humus	Time necessary to clear solution Minutes	Nitrogen found Mg.	Per cent. nitrogen in humus	Time necessary to clear solution Minutes	Nitrogen found Mg.	Per cent. nitrogen in humus
Wilfarth's method.....	25	{ 2.07 2.20 2.17 2.62	3.91	30	{ 7.31 7.21 7.07 8.05	4.86	40	{ 13.27 13.64 13.51 13.05	4.62
Gunning-Atterberg method.....	20	{ 2.34 2.31 3.29	4.40	25	{ 7.70 8.13	5.32	35	{ 13.66 13.87 13.94	4.71
Hibbard method.....	15	{ 3.10 3.33	5.89	20	{ 8.36 7.66	5.57	30	{ 13.66 13.87 14.28	4.82
Salicylic acid method.....	30	{ 3.10 2.87	5.44	40	{ 7.66 7.49	5.14	60	{ 14.21 14.10	4.95

added 12 grams of a salt mixture consisting of 10 grams K₂SO₄, 1 gram FeSO₄ and 0.5 gram CuSO₄, and the solution is digested until the nitrogen is all changed to ammonia. There follow results obtained by the use of humus portions equivalent in the case of Soil No. 1 to 10 grams of the soil, in the case of Soil No. 2 to 1.66 grams of the soil and in the case of the Soil No. 3 to 0.5 gram of the soil. The amounts of nitrogen found in milligrams are given in duplicate or triplicate and the percentages of nitrogen are calculated on the basis of the averages of these amounts. All other data are given in the table below:

In a comparison of the data set forth in the above table, and the experience had in the management of the various determinations we find:

the Hibbard method, in which the digestion proceeded rapidly and quietly in all cases, thus confirming the experience of Hibbard as reported in the paper above cited.

V. The manipulation included in the Hibbard method surpasses in simplicity and speed all the other methods tested, among which are those most commonly used to-day.

In view of the fact, therefore, that the Hibbard method is far superior to the others so far as both accuracy and speed are concerned, we must urge its use in all humus nitrogen determinations.

SOILS RESEARCH LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

LABORATORY AND PLANT

THE MANUFACTURE AND PROPERTIES OF SUBLIMED WHITE LEAD²

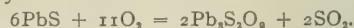
By JOHN A. SCHAEFFER

The manufacture of sublimed white lead, the commercial name for the basic sulfate of lead prepared by the sublimation process, depends directly upon the oxidation of galena, the sulfide of lead, when subjected to intense heat in an oxidizing atmosphere. The combustion under these conditions proceeds with violence resulting in the formation of a white sublimate, which, when purified, is known as sublimed white lead.

¹ THIS JOURNAL, 2, 463.

² Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

The reaction which occurs in this oxidation of galena may be written as follows:



This formula, Pb₃S₂O₇, or 2PbSO₄.PbO, is analogous to the generally accepted formula for the basic carbonate of lead—2PbCO₃.Pb(OH)₂. Commercial sublimed white lead, however, contains a higher percentage of lead sulfate than that required for the above theoretical formula. While the formation of the theoretical basic sulfate of lead is entirely feasible, its manufacture has not proved commercially advantageous. The conditions for the oxidation of the sulfide of lead are, consequently, so adjusted that a compound showing about 16 per cent. of lead oxide is ob-

tained. The conversion of a small percentage of the lead oxide, present in the theoretical basic sulfate of lead, to lead sulfate, undoubtedly results from a reaction between the lead oxide and the sulfur trioxide which forms from the oxidation of a certain amount of sulfur dioxide. A small percentage of zinc oxide is formed at the same time from the sphalerite, the sulfide of zinc, which is present in almost all non-argentiferous lead ores. It is maintained that the presence of about 6 per cent. of zinc oxide enhances the value of the pigment.

Coke of a hard compact variety is used as fuel, while iron, in the metallic form, and limestone serve as fluxing materials together with the silica present in the ore. Any metallic lead which forms from a reduction of the lead compounds by the coke, at the intense heat continually maintained in the furnace, is separated from the readily fusible slag by a difference in their specific gravities.

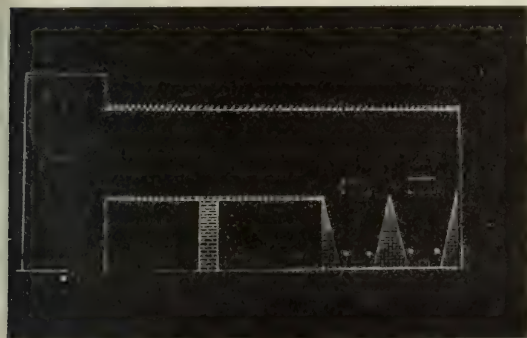


FIG. I—DIAGRAM SHOWING LOCATION OF FURNACES IN RELATION TO COMBUSTION CHAMBER AND "BEEHIVE"

Blue Fume, the fume known commercially as sublimed blue lead, is frequently added to the charge. This fume is formed in the smelting of lead ores and is recovered by the bag room process. It is found to contain about 35 per cent. of lead oxide and about 50 per cent. of lead sulfate. This fume pigment, sublimed blue lead, is rapidly finding extended use as a paint pigment for the protection of iron and steel. Its composition renders it extremely valuable as a charge material and being a product of sublimation it is extremely reactive when subjected to the conditions found in the oxidizing furnaces.

The method of charging the furnaces varies with atmospheric conditions and the life and temperature of the furnace, charges being formulated to meet these conditions.

By following the charge from the raw materials to the finished products, the general working conditions can be best understood.

The oxidizing furnaces, two being considered a unit, consist of oval iron water-jackets, four feet in height, open at both ends, the upper end being five feet in length and three and one-half feet in width.

This water-jacket is securely built in a brick structure, on a solid brick base, and has a small opening in

front which serves as a tap hole for the continuous removal of slag and metallic lead and their separation by the difference in their specific gravities. An oxidizing atmosphere is maintained by blowing air through tuyère holes entering near the base of the furnace. The feed door of suitable size and form is placed at one side of the furnaces.

The brickwork surrounding the water-jacket or furnace proper is extended upward so as to form a large combustion chamber, which is in some cases water-jacketed.

Immediately upon feeding the charge into the furnace, the fire of which is maintained at a point of incandescence, the reactions previously described occur with great violence and the volatilized lead passes upward into the combustion chamber.

Suction is maintained by a powerful fan placed between the bag room and the "goose-necks" which draws the condensed fume onward through the cooling system, finally driving it into the bag room where it is deposited.

The cooling system is built so as to produce maximum cooling effect by the introduction of baffles which prevent the easy passage of the fumes into the bag room. After the fume has passed out

of the beehive, where it is condensed and purified, it is drawn through the "goose-necks," large inverted U-shaped pipes resting on hoppers, by the large suction fans and thence forced into the bag room.

The bag room is of a special type somewhat similar to those used in the collection of all fumes.

In the sublimed white lead bag room, however, are found three rows of hoppers (Fig. V), each hopper carrying 24 bags. The pressure of the fan forces all the gas through the cloth of the bags, while the sublimate is deposited. Occasional shaking throws the fume into the hopper where it is packed for shipment.

Sublimed white lead, as it is removed from the hoppers, is white in color. Much fume, however, which is unsatisfactory and not suited for use in the various arts, is deposited in the portion of the cooling system preceding the suction fan. This fume is contaminated with a small percentage of coke, ash and other impurities, and being of a higher specific gravity than pure sublimed white lead it is readily deposited before reaching the fan, by a careful adjustment of the suction. The fume becomes darker in color the nearer the approach to the furnace. As a charge material the sublimate is excellent, owing to its very finely divided condition.

Sublimed white lead, being a fume product, consists of very fine amorphous particles, in size about

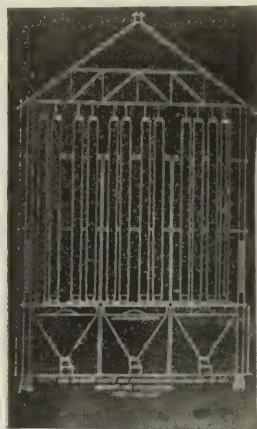


FIG. II—DIAGRAM SHOWING ARRANGEMENT OF BAG ROOM



FIG. IV.—"BEEHIVE" WITH "GOOSE NECKS" IN THE DISTANCE

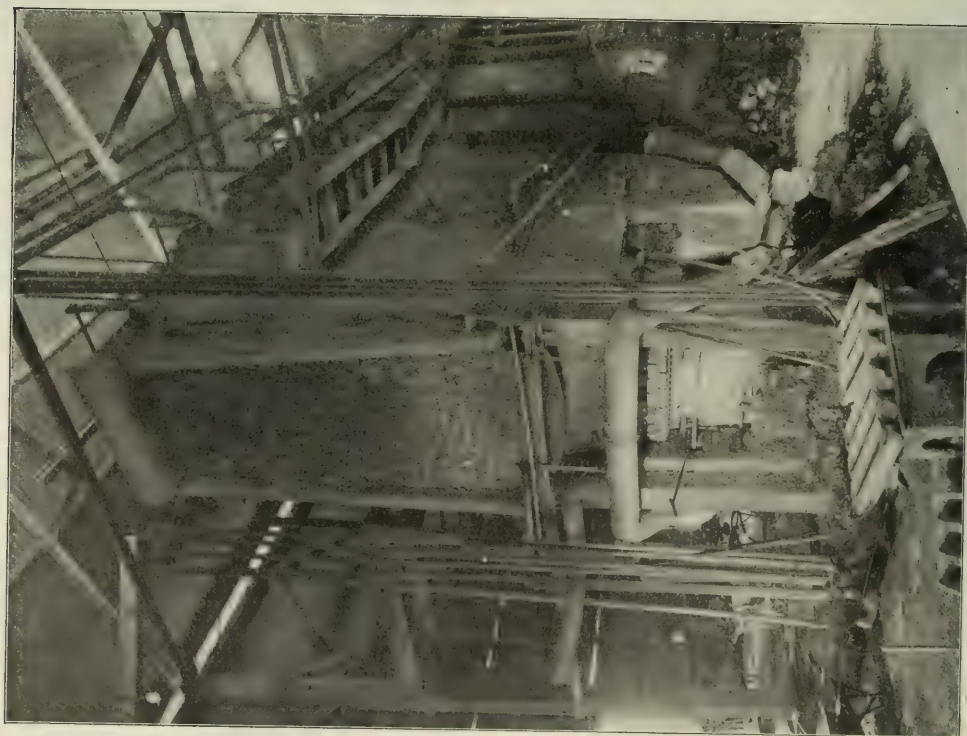


FIG. III.—FURNACE FOR MAKING SUBLINED WHITE LEAD. COMBUSTION CHAMBER ABOVE. TROUGH FOR SEPARATION OF METALLIC LEAD FROM SLAG IS IN FRONT OF FURNACE

one thirty-five thousandth of an inch in diameter. Its specific gravity is found to be 6.2.

In composition it shows approximately 78 per cent. of lead sulfate, 16 per cent. of lead oxide, and 5.5 per cent. of zinc oxide. That the lead oxide present is chemically combined as a basic sulfate of lead, the sulfate of lead present in excess of the amount required for the theoretical formula being present as neutral sulfate of lead, is held by practically all authorities. Chevalier claims the formula of $Pb_3S_2O_8$ for the fume resulting from a furnace roasting lead sulfide.

According to Toch,¹ we find that "A mixture of precipitated lead sulfate, litharge and zinc white in approximately the proportions found in sublimed

est difficulty. It shows only slight darkening in an atmosphere containing appreciable amounts of hydrogen sulfide gas. When used in colored paints containing chemically reactive tinting materials, it exhibits chemical inertness. The tinctorial power and opacity is directly lowered with a decrease in the percentage of lead oxide.

When chalking is noted in paints containing high percentages of sublimed white lead, it is found to differ from that noted in the case of other white lead pigments. According to Holley,² we find: "When ordinary white lead begins to chalk vigorously, it will be found that the paint film has lost its elasticity, and has become brittle and friable throughout; also,

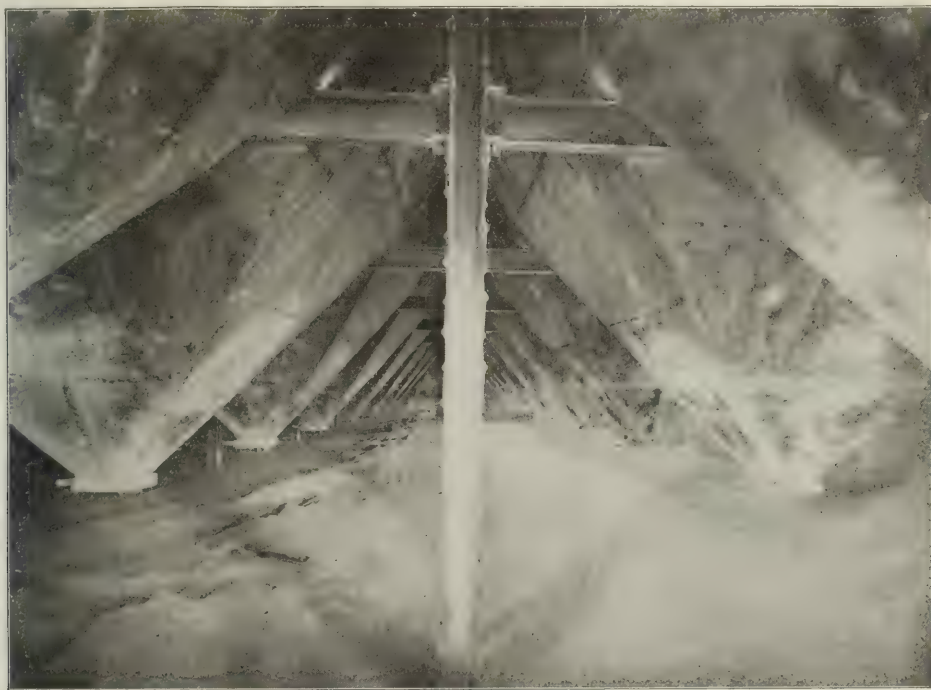


FIG. V HOPPERS INTO WHICH SUBLIMED WHITE LEAD FALLS FROM BAG ROOM

lead, when ground in oil and reduced to the proper consistency, dries totally different from sublimed white lead; in fact, sublimed white lead, when ground in raw linseed oil, takes two days to dry dust free, but the mixture just cited will dry sufficiently hard for repainting in twelve hours, because lead sulfate is a fair drier and lead oxide a powerful one. The oxysulfate having the same composition, behaves totally different from the mixture." A mixture of the neutral lead sulfate with two per cent. of sublimed litharge, the finest and palest oxide of lead yet prepared, shows a yellow color not approached by any sublimed white lead yet made.

When sublimed white lead is subjected to the heat of the blowpipe it is reduced to metallic lead, when intimately mixed with charcoal only with the great-

est difficulty. The luster of the film under the chalk-like coating has entirely disappeared. A sublimed white lead film, on the other hand, retains much of its original elasticity under the chalk coating, indicating that the disintegration is confined to the surface, and it is possible that the retention of the 'chalk' on the surface gives some protection to the unaffected coat below."

The pigment, in common with other white lead compounds, finds its greatest value when compounded with zinc oxide and a small percentage of inert pigment of a crystalline nature, as these pigments tend to overcome those factors which militate against the use of the pigment alone.

Sublimed white lead is a pigment extensively used in the compounding of the finer grades of rubber goods.

¹ "Chemistry and Technology of Mixed Paints," Maximilian Toch, p. 19.

² "Zinc and Lead Pigments," Holley, p. 115.

The pigment has been found to practically inhibit corrosion on iron and steel even after long exposures, and ranks favorably with all other pigments yet prepared for the elimination of this decay. In consequence, it is rapidly finding its predicted place among paint pigments not only as a protective coating for wood but as a preservative for iron and steel.

PICHER LEAD CO
JOPLIN, MO

A NEW FORM OF LABORATORY EXTRACTION APPARATUS¹

By A. E. PERKINS

Received October 25, 1912

The great variety of extraction apparatus now on the market would seem at first thought to supply a form adapted to any purpose; yet, in selecting apparatus for continuous use in a laboratory where large numbers of extractions must be made, one is impressed with the fact that all these forms have in common some of the disadvantages enumerated below.

Most forms of extraction apparatus are very complicated, very expensive and very frail. Nearly all forms have two joints of the cork, ground glass or mercury seal type. These are sources of endless breakage trouble and annoyance, besides furnishing an

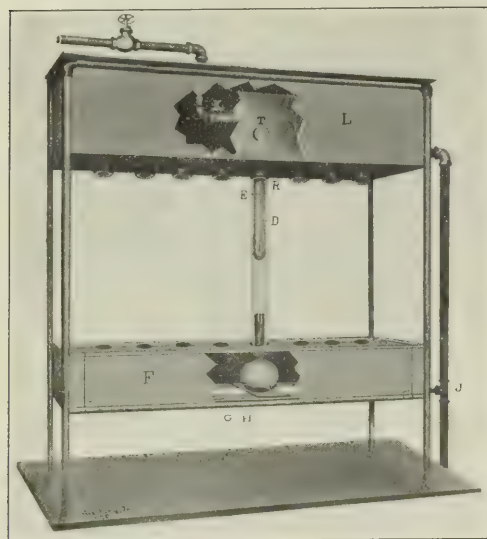


FIG. 1

easy means of contaminating sample or solvent with water leaking from or condensing on the supply pipes. Nearly all the common forms of extraction apparatus must be supplied with water under pressure, which must ordinarily be conveyed to the condenser through rubber tubing. This rubber tubing may frequently break or leak and flood the laboratory, or kink and shut off the water supply; moreover, to keep it in good condition requires continual care and expense.

Efforts by the writer to eliminate certain of these defects from an apparatus to be used in this laboratory

¹ Drawings by Mr. Wm. P. Beeching, Jr.

have resulted in the construction of the form of apparatus which is here described.

The frame supporting the apparatus (Fig. 1) is of $\frac{1}{2}$ inch metal tubing and has approximate dimensions of $36 \times 32 \times 8$ inches, accommodating 8 extraction flasks which are placed $3\frac{1}{2}$ inches between centers.

The extraction flask A (Fig. 3) is flat bottomed and has a diameter of $2\frac{3}{4}$ inches and a height of 2 inches to the base of the neck; the constricted portion of the neck B has height and diameter of about



FIG. 2

one-half inch each; the large upper portion of the neck C has a diameter of $1\frac{1}{8}$ inches and a height of 12 inches. The condenser D is merely a test tube of special shape (9 inches \times $\frac{7}{8}$ inch). The small glass tube E has a diameter of about $\frac{3}{16}$ inch. All glass parts are of rather heavy German glass. The dimensions will accommodate any extraction tube up to 5 inches in length and one inch in diameter. A perforated porcelain, or aluminum plate is used to support tubes of small size.

The box F (Fig. 1), enclosing the lower part of the extraction flask, is of sheet metal about 4 inches high, the front, back and top being hinged so that they can be dropped out of the way, leaving the bottom of the box as an open platform when the flasks are being adjusted. The bottom of this box has an opening, G, three inches wide and extending the entire length of the box, except for two inches at either end. Heat is supplied by steam passing through a $\frac{1}{4}$ inch lead pipe, H, which makes three circuits of the box, being separated from the bottom by a layer of asbestos board. The valve controlling the flow of steam is not shown in the drawing. The $\frac{1}{4}$ inch lead pipe carrying the exhaust steam enters the waste pipe through a Tee joint, J, and extends downward 4 or 5 feet, completely condensing the exhaust steam.

The extraction flask when in position is supported directly over the opening G by a strip of heavy sheet copper 3×7 inches in dimensions, the ends of which rest on the steam heating coil, the copper strip serving also to conduct heat to the flask. When the flask is being put into or taken out of position, the copper

strip is withdrawn and the flask lowered through the opening G until clear of the condenser D.

The supply tank L (Fig. 1) for the test tube condensers consists of two sheet metal tanks placed one inside the other, M (Fig. 2), and separated by an air space. The bottoms of both tanks are provided with collared holes placed $3\frac{1}{2}$ inches between centers, the collars for the inside tank N (Fig. 2) being $1\frac{1}{2}$ inches in diameter and extending downward, those for the outside tank being one inch in diameter and extending upward into the tank thus overlapping as shown.

The test tube condensers are fitted into the collars of the inner tank with rubber stoppers, P (Fig. 2), being wound with fat free paper or cotton to make a close joint with the outer tank O and with the top of the extraction flask R (Fig. 1). The inner tank has a rim $\frac{3}{4}$ inch wide extending entirely around it; this rests on the top of the outer tank and thus en-

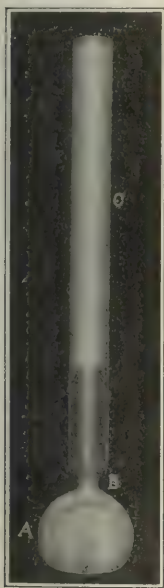


FIG. 3

closes the air space between the two. The inner tank is provided with a partition, V, running lengthwise about two inches from the back wall of the tank, the top of the partition being an inch lower than the top of the tank. Collared holes are provided in the partition S (Fig. 2) two inches above and directly opposite the holes in the bottom of the tank; into these are fitted by rubber stoppers, S and T (Fig. 2), small glass tubes bent downward and extending nearly to the bottom of the test tube condensers as shown in Fig. 1. Water from the supply pipe enters the inner tank back of the partition and when its level has risen above the ends of the glass tubes, flows through them into the test tube condensers which overflow into the front chamber of the inner tank. Any excess of water will flow over the partition.

The water supply pipe is narrowed to a $\frac{1}{4}$ inch opening and provided with a hood as shown in Fig. 1; and the waste pipe U which is jointed to the inner tank by means of a rubber stopper is $\frac{3}{4}$ inch in diameter, thus eliminating the danger of flooding. By closing the waste pipe and allowing the water to stand 3 or 4 inches deep in the tank practically complete condensation of ether is secured for an indefinite period without running water when the room temperature is not unusually high.

Rapid and complete extractions are secured with this apparatus. Fat determinations are most conveniently made by difference, though the flask has no re-entrant surfaces to prevent complete transfer of the extract to another container for direct weighing.

Most of the faults enumerated above have been avoided in this apparatus. Joints of all kinds have been eliminated from the extraction apparatus proper.

No pipes for distributing water to the condensers and no troublesome rubber tubing connections are needed. Contamination of sample or solvent by water has been made nearly impossible. The glassware costs less than one-fourth as much as most other forms of extraction glassware, and being simpler and stronger it is less liable to breakage.

LABORATORY OF DEPARTMENT OF DAIRYING
OHIO AGRICULTURAL EXPERIMENT STATION
WOOSTER

A DEVICE FOR CONTROLLING SMALL ELECTRIC FURNACES¹

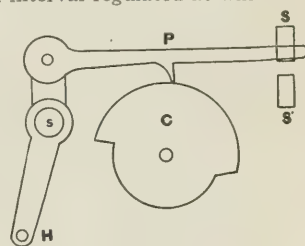
By CHARLES BURTON THWING

The plan described herewith for maintaining any desired temperature in a small electric furnace was devised for use with a 10 kilowatt carbon plate resistance furnace, for which direct current only was available.

It is usual to employ alternating current for such furnaces, reducing the voltage as the resistance of the furnace falls with the rising temperature.

Where direct current is used, the control is usually effected by means of a rheostat, which, of course, wastes a considerable portion of the energy. The present plan dispenses with the use of a rheostat, by automatically opening the circuit once a minute and closing it after an interval regulated at will.

The control is effected by means of a small motor, which drives, by small gears, a cylindrical cam, C, 250 mm. (9.87") long and 50 mm. (1.97") in diameter, the cylinder being cut away on a taper from 350° at one end to 0° at the other.



ELECTRIC FURNACE CONTROL

The pawl P is carried on a screw, S, which can be turned by the handle H to set the pawl quickly and accurately to any desired position. When the pawl is resting upon the cam, the control switch S is closed. This automatically closes the clapper switch carrying the current; when the pawl drops, the control switch S' is closed, opening the clapper switch and cutting off the supply of energy from the furnace.

It is evident that the fractional amount of time during which the current is supplied to the furnace varies with the position of the pawl on the cam. While heating the furnace, the automatic switch is at rest; when the desired temperature has been attained, the motor which actuates the switch is started and the cam set to the position which has been found by trial to furnish the energy required to balance the losses by radiation. The pawl may be set with ease to within 1 mm. (0.03937"), which is, of course, a finer adjustment than is required.

The control of the furnace is further effected by placing in series with the carbon resistance an auxiliary resistance of 0.2 ohm of nichrome tape, which in-

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

increases to 6.3 ohm at the maximum temperature. The furnace is operated at 1300°C . (2372°F), and since this is too high for the nichrome to withstand permanently, the latter is placed in the base of the furnace, where the temperature does not exceed 1100°C . (2012°F). The increase of resistance of the nichrome with the rise of temperature tends to offset, in some measure, the diminishing resistance of the carbons, and so to prevent any accidental overheating of the furnace in case of failure of the operator to look after the adjustment of the controlling device.

The chief advantage of this plan over the rheostat is in the saving of energy. All the energy consumed is delivered to the furnace, except the small amount (about 50 watts) required to run the motor, and the much smaller quantity required to actuate the switch.

PHILADELPHIA, PA.

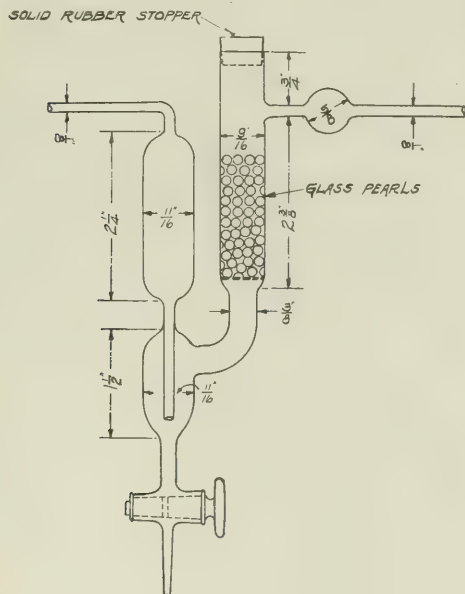
GAS BUBBLE AND WASHING TUBE FOR COMBUSTION APPARATUS

By H. E. SMITH

Received October 21, 1912

For several years I have used in combustion apparatus and for similar purposes a certain form of gas bubble and washing tube which has proved so very efficient and convenient that it may be of interest to other chemists.

The tube is shown in the accompanying sketch. It will be seen that the entering gas bubbles through the liquid in one compartment, then is exposed to a large surface of glass pearls in another compartment.



The especial feature of the tube is that the spent liquid may be drawn out and the tube refilled without breaking the connections with adjoining apparatus

or removing the tube from the train of apparatus. The spent liquid is drawn off by means of the stop-cock after which the tube is recharged by removing the rubber stopper at the top and running in the proper quantity of fresh liquid from a pipette. It first moistens the pearls, then accumulates in the lower compartment.

LAKE SHORE & MICH. SOUTHERN RY. CO.
COLLINGSWOOD, O.

A MODIFIED EXTRACTION APPARATUS

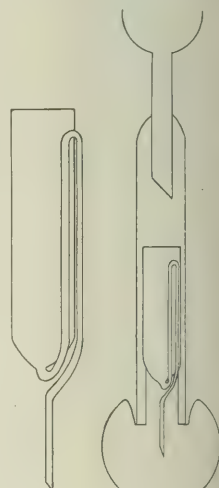
By G. M. MACNIDER

Received October 18, 1912

While there are quite a number of extractors now on the market for determining fat in solid substances, with each form there is some feature which is not entirely satisfactory when a large amount of routine work is to be done.

The Soxhlet and Knorr forms are probably most generally used. The siphon principle of the Soxhlet apparatus has been found to be most satisfactory for general work, but the cork or ground glass joints of this apparatus cause considerable trouble in setting up the apparatus and are frequently the cause of the loss of large amounts of ether. The Knorr form is superior to the Soxhlet in that it requires about one-third the amount of ether for an extraction and has only one joint, which is a mercury seal, thereby preventing the loss of ether. But the percolation principle of the Knorr is unsatisfactory on account of the difficulty in preparing satisfactory asbestos filters. The modified form described below was designed to combine the desirable features of the Soxhlet and Knorr forms.

The apparatus consists of a small siphon extraction tube (Fig. I) which fits into the Knorr adapter in place of the percolation tube used in the regular Knorr apparatus. The extraction tube is 8 cm. long and 2 cm. in diameter. The siphon is sealed into the bottom and rises to within 1 cm. of the top of the extraction tube. The details will be apparent from the cut. The sample to be extracted is contained in a S. & S. extraction thimble which fits closely into the extraction tube. In this laboratory, extraction thimbles 19×90 mm. are used and the thimbles trimmed down to a height of 80 mm. to make them flush with the top of the extractor. The extraction tube is shown in place in Fig. II.



As will be seen from the above, the siphon principle of the Soxhlet apparatus has been combined with the desirable features of the Knorr apparatus. As the extraction tube is small the extraction is done very rapidly so that the apparatus is well adapted to both

commercial work where the extractions must be done in a short time and to more accurate scientific work where the substance is extracted for a longer time.

A set of twenty of these extractors has been in use in this laboratory for about six months and has proved entirely satisfactory with a variety of substances.

FEED AND MICROCHEMICAL LABORATORY
NORTH CAROLINA DEPARTMENT OF AGRICULTURE
RALEIGH

A REFLUX CONDENSER

By S. W. WILEY

Received October 25, 1912

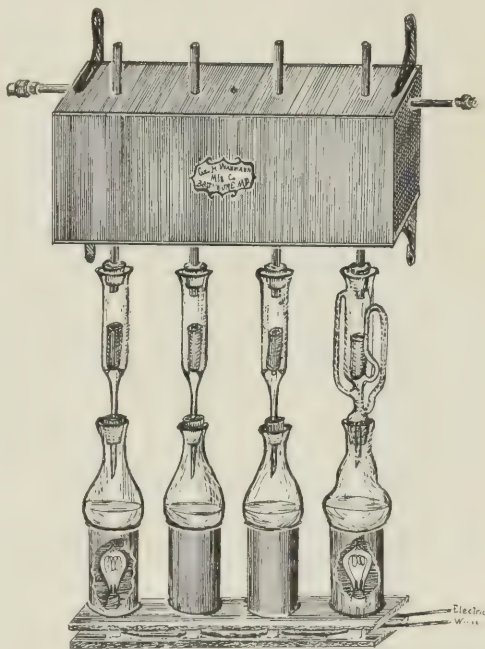
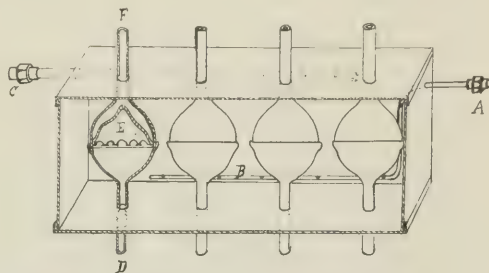
The piece of apparatus discussed in this paper was designed because of the small space occupied by it and the degree of efficiency obtained by its use in comparison with other types now on the market.

This condenser as shown has been used by Wiley & Company's laboratory and has given great satisfaction. We have found it indispensable for extraction with ether or other solvents or for any purpose where a reflux condenser can be brought into use. The cuts show clearly the construction of the various parts and, from a close inspection of the cuts, an adequate idea of the large condensing surface that can be obtained in comparison with the size of the water jacket. The condensing tubes are of block-tin tubing and on entering the water jacket are connected to bell-shaped condensers of spun copper. On entering the bell which is composed of two sections, the uncondensed ether passes through perforations and is condensed on the upper surface of the bell. The condensing surface of this arrangement is over 120 square inches in comparison to the straight tube usually used, two feet being the length that is ordinarily used with an internal diameter of $\frac{3}{8}$ inch which would have a condensing surface of about 25 square inches. The water inlet is so arranged that the water bubbles up and surrounds every portion of the condenser, and by this scheme we have the condensing surface continually exposed to fresh, cold water thus insuring continual condensing of the solvent with a minimum loss.

To this condenser any form of extraction apparatus may be connected and in this laboratory a special form is used, which is simple in construction and at the same time efficient.

For heating the solvent we use the scheme shown

below. The apparatus shown has two decks thoroughly insulated and with a two-inch air space between decks as a safeguard to overheating. The heating is furnished by 16 c. p. incandescent bulbs and a spun



cup, insulated on the outside to prevent radiation, surrounds the bulb and forms a rest for the extraction bulb.

ANALYTICAL LABORATORIES
WILEY & CO.
BALTIMORE

ADDRESSES

TAR DISTILLATION IN THE UNITED STATES—GENERAL DEVELOPMENT AND RECENT PROGRESS¹

By R. P. PERRY

INTRODUCTION

One feature of the general conservation movement which has attracted much attention in recent years is the estimated use and available supply of coal. For years our household and factory fires have been burning cheerfully—although in many cases rather smokily—and we have had an optimistic feeling that our

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

coal mines were inexhaustible. Even now fuel is so plentiful and comparatively cheap in many parts of the country that a large portion of the public forgets that there may be a cold tomorrow. If we travel by night through the Connellsville section we see the glare from thousands of beehive ovens light up the sky and throw picturesque shadows on the hills, but if we study the careful and interesting reports of the United States Geological Survey, we may well be amazed at the apparently reckless annual waste of millions of dollars worth of by-products—gas, ammonia and tar—from these ovens, when converting bituminous coal into coke for the great iron and steel industry. At the same time,

those who are familiar with the conditions abroad wonder why they see there so many orderly piles of coal briquettes utilizing the coal dust or slack with a coal tar pitch binder, while in certain regions here they see abandoned culm banks. The explanation is as indicated above—the past and present generation living for themselves on the easily obtained abundance of our mineral resources, and, if they stop to consider the future, assuming it will take care of itself. Some caustic criticism has been directed at American wastefulness, and it is by no means undeserved, but our foreign friends, who, having more slender coal supplies, raise their hands in righteous horror at our methods, should make due allowance and remember that in some directions the American traveler is equally amazed at the evidence he sees abroad of what appears to him a waste of human labor or of special materials. I can remember, for example, seeing in Germany some miles of solid fence along the railroad made of abandoned steel cross-ties, one end buried in the ground, set closely touching one another. We would hardly understand such fence construction from our experience and point of view. Similarly, the American manufacturer, accustomed to labor-saving devices at home, is almost speechless when he sees the army of porters cumbrously transporting luggage from boat to dock and *vice versa* at the European ports.

In each case there is sure to be some reason, although not always an adequate one, why conditions are as they are. Some little emphasis is laid on this point as it rises again and again in considering the development of the tar industry in the United States, as it inevitably must be considered in comparison with the development abroad, particularly in Germany. For example, the more scientifically interested traveler who has read of the wonderful coal tar dyes, colors, medicines, etc., and may have seen some of the very large factories in Germany, wonders why such products are not made in the United States. If satisfied with the first tabloid answer available, he will recall what the popular scientific magazines have written about the German superiority in chemical lines, and assume that tells the whole story. The brilliant reputation of our good friends, the Germans, is certainly very well deserved, but numerous domestic and international trade conditions have an equal or more important bearing on why the development of the industry has been along radically different lines here and abroad.

Going back to the initial fact that many million barrels of tar literally go up in smoke from our beehive coke ovens, we find there was in the past a well-defined fear of undertaking by-product ovens for several reasons. In the first place, it took much time to overcome the incorrect feeling that for some intangible reason metallurgical coke was better when made in beehive ovens. Also it was feared there would not be a market for the tar product which would be sufficiently large and remunerative. Both of these fears have now been overcome, as the successful use of by-product coke has become a fact in the most progressive furnaces, and in general the tar industry has taken up the greatly increased production.

Successful working up of the tar commercially here depends upon finding a profitable use for its main constituent, pitch, as there has been a much greater demand for the oils and the products derived from them than our domestic supply. The foreign use of pitch is mainly as a binder for coal dust or slack in making briquettes. There has recently been a very appreciable development of briquetting in certain sections here, but a curious argument in a circle is still heard at times. On the one hand, some coke operators have said there was no market for additional tar because there was no briquette industry and at the same time briquetting interests have regretted there was no assurance of an adequate supply of pitch binder because the limited output of tar distillation went to make pitches for other purposes which would bear a higher price. Between the two stood the tar distillers, ready and anxious for additional business, but as usual

there were other economic conditions having a most important influence.

In many places bituminous lump coal is still so comparatively cheap and abundant that briquettes could not compete and the market for domestic briquettes from anthracite dust is also somewhat limited. In some cases the geographical location of tar production and possible pitch consumption are so far apart that railroad freights are an insuperable barrier.

Another present and potentially very large use for tar products is in making bituminous road binders, as covered in other papers. I will only mention in passing that although this development in the United States is extremely satisfactory, yet there are very large supplies of petroleum products and residues designed for road work at low prices, whereas these conditions are reversed abroad, particularly in Germany. In fact, the great increase of road tar abroad has tended to divert much tar, leaving a shortage in the briquette pitch field.

As regards dyes, colors, medicines, special chemical products, etc., derived from coal tar, the conditions are peculiar. Most of these are derived from benzol, phenol, cresol, naphthalene and anthracene. Figured on the original tar these total only a relatively small percentage. Further, the finer products require numerous intermediate steps, involving more or less labor, as well as extensive chemical treatment with acids and alkalis. The price of labor abroad, including trained chemists, would probably average not more than about half that paid in the United States. The question as to what the smaller wages will purchase relatively in the way of rent, food, clothing, etc., is an interesting economic study, but does not alter the fact that to the manufacturer the labor costs very much less and enables him to produce cheaper in this respect. In many cases, also, he has an advantage in cheaper chemicals, which play a very large part in the cost of the finished products, running from about fifty per cent. upwards. Another most important feature is the patent situation. Many of the finer products derived from coal tar are covered by United States patents held directly or indirectly by a small group of German interests. Dr. Bernard Herstein has recently analyzed this situation in an interesting way.¹ Perhaps one most essential point is that existing United States patent law (differing from that of most foreign countries) permits patenting of the product as such as well as any particular means of production, and further, there is no requirement that the product be made or the process used in the United States. In other words, the German group can and does control a large number of United States patents on these products, and having this protection it is under no necessity of employing American labor or capital in manufacturing here, but can ship to this country from Germany or elsewhere, subject only to tariff regulations. The injustice of a similar situation has recently been recognized by Great Britain which adopted a compulsory working act, with the result that many foreign firms promptly built factories in England. The matter is very important in connection with the features mentioned, producing lower manufacturing costs in Germany. It seems probable, however, that with due justice to inventors, a proper revision of the patent laws will be accomplished before long.

One further rational explanation of why these finer products have not been produced here is that generally there have been uses for the crude or semi-refined products here which netted considerably more than the fine products would have secured. Naturally the tar industry has developed along the lines of least resistance, but already a beginning has been made here in the direction of the finer products, and many of these can be available as fast as there is a demand at prices permitting their manufacture under our conditions. Wherever mechanical handling and machinery plays an important part the United States probably has some advantage.

¹ Address before Society of Chemical Industry, New York, April 19, 1912.

SOURCES OF TAR, AND ESTIMATED QUANTITIES

In the discussion so far, I have referred only to the supply of tar from by-product coke ovens, as this is much larger at present than gas works tar and growing much more rapidly. The earlier coke ovens were built near the mines and steel works in Pennsylvania, but they have followed the blast furnaces as these have moved to the large distributing centers—it having been found better to haul the coal to such points instead of the coke. Such, for example, is the recent very large development near Chicago, there being by-product ovens at Gary, Joliet, South Chicago and Milwaukee. More recently, under peculiarly favorable conditions of supply of raw materials for iron and steel manufacture, some large coke oven plants have been erected near Birmingham, Alabama. There are many others distributed throughout the eastern half of the United States, some of them located where they can supply illuminating gas to large cities, and others use their surplus gas in open hearth furnaces or other parts of the steel plant. As distinct from by-product ovens, the gas works are located always in the cities, the largest producers of gas works tar being in New York, Chicago, Philadelphia, etc. Most of these gas works produce both coal tar and water gas or oil tar. The differences of quality will be considered later. In some sections of the United States the abundant and cheap supply of natural gas has temporarily, at least, made the operation of gas works financially impracticable.

It is somewhat difficult to get complete data of production of tar, especially of the gas works grade, but it seems probable that, including coke oven and both kinds of gas works tar, the 1912 production in the United States may not be very far from 165,000,000 gallons, of which about two-thirds is coke oven tar. In comparison with this, it has been estimated¹ that if the remaining beehive ovens were converted to by-product ovens, there would be an annual increased production of perhaps 735,000,000 gallons. That the development in this direction has been recently very strong is indicated by the fact that within the year ending in September new by-product ovens have begun operations turning out approximately 35,000,000 gallons of tar per annum.

QUALITY OF VARIOUS TARs

Depending upon the coal used, and more particularly upon the size and shape of retorts, the travel which the gases make over the hot surfaces, and the temperatures to which the gas is subjected, the coal tars vary within wide limits. In general with the vapors subjected to the higher temperatures usually characteristic of gas works as compared with coke works, there is an increase in specific gravity and free carbon. For example, the tar from many gas works will average about 1.24 specific gravity at 15.5° C. (60° F.) and about 25-30 per cent. free carbon by weight, whereas from the by-product coke ovens the specific gravity would average more nearly 1.19 and the free carbon would vary about 5-18 per cent., the average being less than 10 per cent.

The so-called free carbon represents a finely divided inert material, largely carbon, which is the portion of tar insoluble in benzol and toluol. Perhaps a very small part is carried over mechanically in the coking process, but for the most part it is due to the cracking of the hydrocarbons by exposure to heat, and the higher percentage usually found in gas works tars is from this cause. All gas works tar does not contain a high percentage of free carbon, as I found that in one of the largest European gas works the free carbon in the tar was only about 10 per cent., the percentage having been reduced very much from former figures by increase in the charging of the retorts and some other operating changes. There has recently been some development of the use of inclined and vertical gas retorts in the United

States, some of which produce tars lower in free carbon than many coke ovens.

The free carbon test of the various tars is very important because the percentage has a very considerable influence on the pitch product, and, moreover, it is an indication, to a certain extent, of the quality of oils and bitumens forming the balance of the tar. For many years there was very little coal tar produced in this country, except from gas works operating at very high heats, and the tar was extremely viscous, of high specific gravity and often containing from 30-40 per cent. free carbon. It was very difficult and expensive to distil such tar, because of the large percentage of water which is always contained and the tendency for excessive carbon to coke on the still bottoms and cause them to burn out. Because of this extreme, the lower carbon coke oven tars were welcomed as of relatively better quality, but to-day they are not necessarily more valuable as they yield pitches which are extremely subject to temperature influence—being very brittle when cold and easily flowing when heated—and therefore unsuitable for many pitch uses in the United States. The present vastly preponderating amount of very low carbon tars in many places is an extreme as unsatisfactory at times to the tar distiller as was the very high carbon gas tar. Much of the skill of the successful distiller is directed to a very careful study of the various tars he has to handle, the selection of each for the purpose for which it is best adapted, and the judicious combining of various tars to produce physical and chemical properties not possessed by any one of them separately.

The oil tars or water gas tars being largely produced from the petroleum oils used in making and enriching gas represents entirely different physical and chemical characteristics, containing compounds of the olefine series as compared with coal tar containing compounds of the aromatic series. In general they are much thinner and more oily than the coal tars, the specific gravity averaging about 1.07 at 15.5° C. (60° F.) and the free carbon about 1 per cent. The pitches produced from these tars, as might be expected, show, to a much higher degree, the properties of brittleness and susceptibility to temperature changes, and the oils have not given the very great value for timber preservation which is characteristic of the coal tar oils. For these reasons the water gas tars have been much less valuable commercially than coal tars and a large amount has been used as fuel. It is to be hoped and expected that further study will find special fields for the use of water gas tar and its products.

There are some small amounts of various other tars made, such as producer gas tar, lignite, wood tar, etc., but as yet these are not commercially significant, although some of them may develop considerably in the near future.

NUMBER AND LOCATION OF DISTILLING PLANTS

There are probably not more than about 40 tar distilling plants in the United States, most of them being naturally located near the producing sources in the section east of the Mississippi and north of the Ohio rivers. The tars will average to weigh about 9½ pounds per gallon and the freights from the gas or coke works are often 25-40 per cent. of the value of the tar at the shipping point, and for this reason there are many small distilling plants designed to take care of the output from only one or two local sources. At the same time there are large distilling plants in such cities as New York, Chicago, Philadelphia, Boston, Cleveland, Pittsburgh, St. Louis, etc.

TRANSPORTATION

Most of the tar in the United States is handled in steel tank cars of about 10,000 gallons (45 to 50 tons) capacity, such cars being largely owned by the distilling companies because of the need of specially designed equipment which the railroad companies do not furnish. These tank cars are of the usual horizontal cylindrical type, about 7 to 8 ft. in diameter and 28 to 30 ft. long, equipped with a dome on top and outlet valve in the

¹ Figured from data in chapter on "Coke," by E. W. Parker, "Mineral Resources of the United States, 1910."

bottom. As tar becomes very thick when cold, it is necessary to have an effective system of steam pipes for heating when unloading. The breakage of these coils—due largely to severe shocks in transportation—is a very troublesome and expensive experience. Where conditions permit, water transportation is used in harbor and sea-going barges from 25,000–300,000 gallons capacity or more. These boats are divided like oil boats into various compartments and equipped with steam coil systems and powerful pumps. In some cases the tar is handled through pipe lines from the producing plant to the distilling works, but long pipe lines, such as are used in handling petroleum oils, cannot be used with coal tar on account of the much higher viscosity of tar, especially when cold.

RECEIPT AT DISTILLING PLANTS

From the tank cars or boats, the tar is pumped (after being heated so as to render it more fluid) into storage tanks of varying sizes, generally from 250,000 to 2,000,000 gallons capacity. The large tar plants require many of these tanks so as to keep the various grades of tar separate, there being often four or five main grades and other special ones from time to time. These storage tanks are generally of steel bottom and sides, the roofs and roof supports being of wooden construction as steel roofs are subject to rapid corrosion. The wooden roofs are covered with built-up roofing of felt, pitch and slag or gravel. These tanks sometimes have steam coils covering the entire bottom, but more often only a small section around the outlet suction to permit warming the tar as rapidly as required to supply the pump. The tanks have small outlet cocks on the side distributed from the top to the bottom, so as to permit drawing off as far as practicable any water which was separated from the tar.

USES OF CRUDE TAR

Just as there existed a preference in favor of beehive coke, so for many years crude tar as received from the gas or coke works was preferred for some purposes, but a rational study has shown that the water and ammoniacal liquor contained in the tar are detrimental and only a small amount of tar is now being used in the crude state, except in such cases as the tar is used for fuel.

DEHYDRATION

It has long been recognized that one of the most troublesome and expensive steps in tar distillation is the removal of the water which is intimately mixed with the tar as received from the gas or coke works. The gas works tar is more troublesome because it contains a higher percentage of water, and at the same time the water is more difficult to remove because the tar is of greater viscosity and contains more free carbon. Many of the coke oven tars will average between 3 per cent. and 6 per cent. water, and the gas works tars between 4 per cent. and 10 per cent. water, although both kinds sometimes contain very much more, up to 40 per cent.

Two main facts to bear in mind explaining why the presence of water is so troublesome are: First, water at 100° C. (212° F.) when changing into steam increases in volume 1646 times, or in other words, a cubic inch of water becomes nearly a cubic foot of steam.

Second, water has the highest known specific heat. Dry tar has a specific heat of about 0.3 to 0.4, depending on the temperature and specific gravity. It will be noted, therefore, that it requires about three times as much heat to raise one pound of water 1° as it does one pound of dry tar.

Many methods have been used to dehydrate tar, perhaps the oldest one being that of allowing it to settle in storage tanks and depending on its lighter specific gravity to cause the water to rise to the surface. This process is aided by heating, intermittent heating with periods of settling being better than continuous heating. Steaming in large storage tanks is, however, very expensive on account of the great loss by radiation, and at best separates out only a portion of the water, particularly with gas

works tar. Other methods have been tried, such as centrifugal machines, squeezing the tar between heated rolls or in tanks under pressure, etc., but have not been commercially successful. The plan most in favor is that of heating the tar continuously in thin films under partial vacuum. This method ordinarily reduces the water to less than one-half of 1 per cent. Special dehydrator apparatus is in use at some of the large works having a capacity of about 50,000 gallons in twenty-four hours.

STILLS

After the tar has been dehydrated it is pumped to intermediate insulated storage tanks and thence as required to the stills for making the numerous grades of prepared or refined tars, soft, medium or hard pitches. Contrary to the German and English practice of using vertical stills with concave or convex bottoms, the still development in the United States has been mainly along the lines of horizontal cylinders. Quite a number of vertical stills have been used for particular conditions and have certain valuable characteristics. Many of the German stills up to recently held from 20 to 30 tons of tar, but the usual stills in the United States hold twice as much or more. One fact which is said to be largely responsible for the smaller unit abroad has been their desire to avoid night operation, whereas it is quite common with us. It seems quite probable to me that before very long we shall have in our large works in the United States three eight-hour shifts, with continuous running of the stills day and night, certain other portions of the works, however, operating only in the daytime.

Different types of brick still settings have been used with the general purpose of avoiding overheating and burning out the still bottoms and at the same time getting the maximum heat efficiency from the coal, liquid or gas fuel. Depending upon the local conditions and the quality of the oils and pitch desired, the stills are run with mechanical, steam or air agitation, or vacuum in addition to the usual heating. The temperature reached in the liquid in the still depends on the grade of pitch desired, the higher temperatures causing more oil to be distilled off and leaving a harder pitch, but the highest temperature does not usually exceed 400° C. (752° F.). The operation of these stills is intermittent, consisting of charging, distilling off the desired amount of oil, removing the residue by gravity, blowing or pumping, and repeating. Continuous stills have certain theoretical advantages, but have not been adopted in practice in the United States. Successful continuous distillation requires a uniform grade of tar and a demand for a very large amount of one grade of pitch for uses which permit quite a little latitude in range of melting point. Several continuous processes have been tried abroad, but have not met with general success, although I know of one very large plant where one continuous process is reported to have been operated with good satisfaction over several years at low cost. In many cases there has been too much fluctuation in the test of the pitch and oil product, but I feel sure the continuous process will come under conditions likely to develop in the future in this country.

OILS, CONDENSATION, USES, ETC.

The vapors escape from the still through a large vapor pipe to the condenser coils. All of the vapor pipe and preferably all of the coils should be made of flanged cast iron pipe using thin asbestos gaskets. In any case, it is necessary to use cast iron pipe as far as one or two turns below the water in the condenser tank, for the reason that certain of the vapors, particularly some of the ammonia compounds in the vapor form, attack wrought iron or steel very strongly, but have comparatively little action in the condensed liquid form. This is one reason why the tops of the stills sometimes eat through before the bottom. Most of the tars at present contain much less ammonia compounds than heretofore, as the ammonia is for obvious reasons recovered at the gas works or coke works.

The condenser tanks are usually square or oblong, with similarly shaped coils, the pipes ranging from six inches down to three inches. The length of the coil depends on the size of the still, the temperature of the available water, etc. The condensed oils are collected and measured in small steel tanks of about 100 to 400 gallons capacity, depending on the size of the stills and other conditions. These small tanks are provided with sight glasses and empty by gravity into a manifold pipe system leading to various large receiving tanks. From three to five fractions are usually collected, such as light oil, carbolic oil, middle oil, heavy oil and anthracene oil. The percentage of each fraction varies with the tars used and the commercial requirement for the oils, and no exact figures can be given. The total per cent. of oil secured in making pitch is generally from 20-50 per cent. by weight. From the receiving tanks the oils are pumped to large storage tanks for shipping or further refining.

The light oil, that having a specific gravity lighter than water, is separated from the water and then used as crude solvent in paints or for cleaning greasy gears, etc., or it is refined to benzol, toluol, solvent, naphtha, etc.

The carbolic fraction is usually collected so as to give the maximum yield of tar acids consistent with getting at the same time as liquid an oil as practicable. The carbolic oils, crude or redistilled, are cooled by natural or artificial refrigeration to remove excessive naphthalene and sold as crude carbolic acid for disinfectant manufacture. Inasmuch as from most tars the carbolic oils seldom contain more than 10-15 per cent. tar acids, and the usual standard required is 20-25 per cent., it is necessary to add extra acid as required. This is obtained by extracting the acids from other carbolic oils, or the middle and heavy oil fraction. The extraction process is a simple one of treating the oil under suitable temperature conditions with caustic soda solution, separating the sodium carbolate and throwing the acids out with sulfuric acid or more commonly with carbonic acid gas. The extracted acid is then redistilled and separated into carbolic acid and cresylic acid. The former is the basis for the purified crystal acid.

The demand for disinfectants is increasing with the campaign to reduce infectious growth and many excellent grades have been made for years, but at the same time many grades have been made unskillfully and are of no real value beyond the psychological one of having a good healthy odor. Just as a standard of purity or strength is required for foods, drugs, etc., it is reasonable to have a standard of efficiency for disinfectants, and the standard most widely recognized is the Rideal-Walker method of comparing with pure phenol under special conditions.

The large use for the middle, creosote and anthracene oils is for wood preserving, and they are fractioned so as to meet the various specifications of the wood preservers. This industry is a very large one and growing rapidly, as the conservationists have pointed out to large users of timber the definite fact that the local supply is gone and the more distant forests are being rapidly depleted. The railroads were among the first to appreciate the situation. Many of the large systems have had timber-preserving plants for years and now very few are without one or more of such plants. Other papers cover this creosoting industry, but in this connection it is of interest to note that the supply of creosote oil in the United States is much less than the demand, and the importations largely from England and Germany during the year 1911 were about 45,000,000 gallons.¹ This quantity represents, perhaps, about two-thirds of the total consumption. Recently there has been a very large increase in the use of creosoted wood blocks for paving as they make an ideal pavement under many conditions, particularly where a quiet pavement is desired in the business sections of large cities. Also there is an increasing demand for the higher distilling grades of creosote oil suitable for surface treatment of wood

(preferably by the hot and cold tank method), and high-grade domestic oils are now produced in large amounts.

Another use of creosote oils is for shingle stains, either plain or with colors. The use of certain fractions for Diesel and similar internal combustion engines in Germany has not developed here as yet because there are other more remunerative uses and in this special field there are various cheap petroleum products.

REFINED TARS AND PITCHES

Depending upon the amount of oil distilled off, we have as the residue in the stills either thick viscous tar or soft, medium or hard pitch. Sometimes the point for stopping distillation is determined by the still temperature or by the amount and test of the oil distillate, but such is possible only with a uniform grade of tar, and more generally samples are drawn from the still itself and tested, the distillation being continued until the desired grade is secured. The usual test is for melting point, which is determined by various arbitrary tests, as there is no such thing as a true melting point of a pitch. A general classification according to the half inch cube melting point would be as follows:

Distilled tars having a melting point less than 32° C. (90° F.).

Soft pitch having a melting point from 32° C. (90° F.) to 49° C. (120° F.).

Medium pitch having a melting point from 49° C. (120° F.) to 71° C. (160° F.).

Hard pitch having a melting point from 71° C. (160° F.) to 99° C. (210° F.).

Very hard pitch having a melting point from 99° C. (210° F.) upwards.

When the right grade has been secured the distillation is stopped and the still emptied either by blowing the contents direct from it by means of dry steam, or by drawing the contents by gravity to a special tank from which it is blown as before to storage tanks or coolers. From these the refined tar or pitch is later loaded into tank cars or tank wagons, or run into barrels, iron moulds or pitch bays, depending upon conditions.

Various grades of refined or prepared tars are made for road binders, for mixing tar concrete used under wooden floors in factories, for painting felt roofs and for saturating dry felt in making the various kinds of roofing paper. The grades are usually determined by specific gravity, distillation, free carbon viscosity, penetration, evaporation, etc.

The soft pitches are used for road binders, and alone or in combination with tarred felts for waterproofing the foundations of buildings, etc. In addition to the tests above, the so-called melting point is noted.

The medium pitches are very largely used for constructing "tar and gravel"—more properly "pitch and felt" roofs used on nearly all large factories having comparatively flat roofs. The construction consists of applying alternate layers of tarred felt and coal tar pitch, the laps or joints being broken and the top layer of pitch having embedded in it clean gravel or crushed slag. The standard construction to-day calls for at least five layers of felt besides the usual layers of pitch and gravel or slag. Other large and growing uses are that of paving pitch for filling the joints of brick, stone and granite pavements, and for waterproofing bridges, etc. These grades of pitch are usually shipped in barrels.

The hard pitches are most largely used for briquetting coal dust or slack. This promises to become a very large industry in the United States later on when lump coal is more expensive, and has already become well established in certain sections where briquettes are made from anthracite dust for domestic use.

The very hard pitches are used for electric carbons and batteries, for insulating, for making "clay pigeons" or "flying black-birds" used for target shooting, for making core compound used in foundries. These pitches are so hard that they can be ground to powder. The hard pitches are run hot either into iron moulds

¹ House of Representatives Report No. 326, p. 65.

or into pitch bays or pits and there allowed to cool. The iron molds can be emptied when cold and the pitch can be dug or mined from the bays and is handled to cars for shipment. Most of these hard grades are shipped in bulk so as to save packages and the freight on same.

ROOFING PAPER

One important branch of the tar industry is the manufacture of roofing felts, largely a mechanical process and therefore one in which we are further advanced here than abroad. The felt forming the basis of these roofings is made from mixed old woolen and cotton rags, largely cotton, along the lines similar to other paper manufacture. Various widths are used, generally thirty-two inches or thirty-six inches, and the paper varies in thickness from the No. 15 to the No. 80 of the paper-maker's scale, weighing from 3.1 to 16.7 pounds per one hundred square ft., single thickness. This felt is made in large rolls weighing about 400 to 600 pounds.

The simplest form of manufacture is the saturation of such felt by passing the sheet continuously through a bath of refined tar, then through revolving squeeze rolls, which remove the surplus tar, and the tarred felt is wound into measured rolls often containing 400 to 500 square ft. This kind of tarred felt is largely used in the "felt and pitch" roofs and also for waterproofing and sheathing purposes.

The so-called prepared or ready-to-lay roofings are of many different kinds, one standard form consisting of two or three layers of tarred felt cemented together with pitch and having a plain surface or one covered with pitch or composition into which, while hot, is embedded crushed feldspar or small pebbles.

REFINED PRODUCTS

The refined products, as noted above, are largely of the general benzol, naphthalene, anthracene group. Much more crude benzol is now obtained by washing coke oven gas in oil scrubbers than is obtained from coal tar distillation. This gas oil or the light oil from distillation is redistilled, treated with sulfuric acid, washed, treated with soda and then distilled with steam. Fractions are collected distilling within certain limits, such as pure benzol, 90 per cent. benzol, toluol, xylol, etc. These are very largely used in this country as solvents, especially in paint and varnish lines, for making varnish remover and as a basis for nitrobenzol, aniline, etc.

Crude naphthalene is purified by crystallizing, passing through centrifugals to remove the oily portions, distilling, treating with sulfuric acid and crystallizing or subliming.

Large amounts are used for moth balls. Specially purified naphthalene is the raw material for making many coal tar colors, this line being hardly touched in the United States, for reasons noted above. Recently some new wax products have been introduced having peculiar dielectric properties, and promise to develop an important field. These are made from naphthalene by a chlorination process.

Anthracene as the basis for alizarine was of great importance at one time, but is not largely purified at present because of the low market price.

Although brilliant chemists have been studying tar products for years, yet the number of constituents and the innumerable combinations which can be produced by treating them with other compounds leaves plenty of opportunity for the future. The recent opening up of various pressure, electrolytic and catalytic processes will probably give us more astonishing products from tar than any yet secured, each success stimulating the world of scientists to further efforts. That the United States will ultimately take a prominent position in the industry is to be expected from the future great supply of tar in this country, and the energy of her students who admire the success of the German, English, French and Swiss chemists and are determined,

if possible, to go one or more steps further. Fortunately there is ample room for all in this fascinating line of work.

NEW YORK CITY

DISPOSAL OF SEWAGE WITH RECOVERY OF ELEMENTS OF PLANT FOOD FOR USE IN AGRICULTURE

By WILLIAM McMURTRIE

Received October 9, 1912

The hygienic disposal of the excremental dejecta of the human population of cities has long been a difficult and troublesome problem, and the best minds of the engineering, chemical and biological professions have been taxed in its solution. It is the purpose of this paper to treat the subject from the chemical standpoint and to call attention to means whereby the organic and other constituents of excremental dejecta of value for plant food may be, in some measure at least, removed from sewage and recovered for use in agriculture.

The desirability of some method whereby this may be satisfactorily and economically accomplished has long been acknowledged and much work has been done with this end in view, but thus far the results have not been altogether encouraging. The importance of recovering the elements of plant food from this source has been recognized by many of the great economists of the world and much thought, effort and means have been devoted to it. In his memorable address to the Bristol meeting of the British Association for the Advancement of Science in 1898 Professor William Crookes said: "There is still another and valuable source of fixed nitrogen. I mean the treasure locked up in the sewage and drainage of our towns. Individually the amount lost is trifling, but multiply it by the number of inhabitants and we have the startling fact that in the United Kingdom we are content to hurry down our drains and water courses and into the sea, fixed nitrogen to the value of no less than 16,000 pounds sterling per annum. This unspeakable waste continues and no effective and universal method is yet contrived for converting sewage into corn. Of this barbaric waste of manurial constituents Liebig, nearly half a century ago, wrote in these prophetic words: 'Nothing will more certainly consummate the ruin of England than a scarcity of fertilizer; it means a scarcity of food. It is impossible that such a sinful violation of the laws of nature should forever remain unpunished; and the time will probably come for England sooner than for any other country, when, with all her wealth in gold, iron and coal, she will be unable to buy one-thousandth part of the food which she has, during hundreds of years, thrown recklessly away.'"

What Professor Crookes has so ably said regarding Great Britain is equally true of the other countries of the world. It would be an interesting study to work out the relation between the fall of the Roman Empire, and the sterilization by continued and consecutive cropping of the wheat fields of the great Campagna and other parts of Italy, the impoverishment of Greece, Turkey and Syria and the wasteful and unintelligent use of the great sources of their supplies of food and clothing, and at the same time to work out the relation of the prosperity of the modern nations to the intelligent management of their agricultural resources. While the people of the United States are earnestly considering, as a nation, the conservation of natural resources it would seem equally important to give no less attention to the conservation and utilization of the wastes, not only of the cities but also of the farms and forests. It would be a study of fascinating interest and well worthy of the thought and effort of our statesmen and economists. Reference has frequently been made in the economic literature to the practice in China of gathering scrupulously all human excreta for use on the farms, and the consequent maintenance of the fertility of the soil for centuries. It behooves us of the professedly more civilized nations, to take some lessons from our neighbors

across the Pacific and utilize our wastes as they have theirs.

While it is possible that the estimate of Professor Crookes is fairly generous it is quite likely that in his estimate, he applied the available data regarding human excreta—including both feces and urine—to the entire population of the United Kingdom and not simply to the urban population connected with sewage systems. It must be borne in mind that the sewages of England and of the European continent are considerably more concentrated than are those of the United States. In considering the waste carried off in sewage the data should be applied to urban population alone. If the excreta of the rural population are wasted it is the fault of the producers. Estimates similar to that offered by Professor Crookes made for the United States and based upon data from various sources are not as striking as those given by the eminent English scientist but they are both impressive and interesting. According to the last census the urban population of the United States in 1910 was 42,623,383, and at the present time must be approximately 44,000,000. To arrive at a reliable conclusion regarding the manurial value of the excreta of this great population, as great as that of the whole of either England or Germany, is not easy because of the lack of reliable determination and records of the amounts of excreta produced and the composition of the product.

Perhaps no authority has given closer attention to the disposal of sewage than Ferdinand Fischer, the eminent German technologist of Göttingen. According to this authority the weights of feces and urine and the contained nitrogen and phosphates from one thousand persons amount annually to

	Feces Quantity Kilograms	Urine Quantity Kilograms
Total weight.....	33,166	428,190
Contained nitrogen.....	489	3,482
Contained phosphate.....	687	1,725

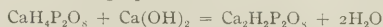
If we accept these figures as representative of the quantity and composition of the fecal excreta of the urban population of the United States the results are interesting. For we may consider that the citizens of the United States are at least as well fed as those of Germany and the quantity of excreta produced should, therefore, be no lower. On this basis we must conclude that the 44,000,000 urban population of the country produces annually dry fecal matter containing over forty-seven million pounds of nitrogen which at 15 cents per pound represents a value of over seven million dollars. This, of course, takes no account of the phosphoric acid which should also be recovered in the process we are about to suggest. If we add to the above figures those for phosphoric acid in feces and urine, which would also be recovered by the process in question, we have an additional total per annum of \$8,800,000. This makes a grand total value of almost sixteen million dollars for the plant food annually recoverable from the urban sewage of the United States. According to another eminent German authority, Heiden, quoted by Storrs in his work on agriculture, the nitrogen voided in human feces amounts per annum to 1.7 pounds per capita, and the phosphoric acid voided in both feces and urine amounts to 2.6 pounds per capita. On this basis the figures named would be even higher.

Yet the figures we have given, based upon data from different sources, are reasonably correct and may, we think, be accepted as fairly representative of what may be expected from the careful and intelligent treatment of the sewage of the United States. In view of the importance of the conservation of our resources it would seem eminently desirable that means should be adopted for the conservation of this source of wealth otherwise destroyed and lost.

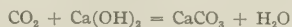
We come then to the method proposed for the removal of the suspended matter of urban sewage and its recovery for use in agriculture. Many methods have been proposed and applied, from broad irrigation and plain sedimentation, to the various

methods of chemical precipitation. Much prejudice has been expressed against chemical precipitation because of inefficiency of clarification, the interference of excess of precipitants with the septic purification of the effluent, and the slight value of the sludge for use in agriculture. All this indicates that care must be exercised in the application of any precipitant. Aluminum sulfate so largely used, when used alone is effective only in very hard waters whose hardness is due to the presence of carbonates, yet it has been frequently used in sewages resulting from the consumption of waters practically free from hardness. Ferrous sulfate has been extensively employed in conjunction with lime, the ferrous hydroxide formed serving as the coagulant to precipitate the suspended matter, but it frequently happens that in order to preliminarily dry the sludge by removal of liquid water in the filter press, excess of lime is used to the extent that a large portion, at least, of the nitrogen is expelled in the form of ammonia, the agricultural value of the sludge is consequently reduced, and the operation of clarification made very offensive.

The precipitant here recommended is acid calcium phosphate ($\text{CaH}_2\text{P}_2\text{O}_8$), commercially known as superphosphate of lime, in conjunction with lime. The acid calcium phosphate (produced by the action of sulfuric acid on tri-calcium phosphate) which may be used as such or in admixture with free phosphoric acid is added to the sewage and thoroughly mixed with it. When the admixture is complete and the solution is homogeneous, lime in the form of milk of lime, $\text{Ca}(\text{OH})_2$, is slowly added, with simultaneous vigorous agitation of the liquid, in quantity sufficient to meet the demands of the reaction indicated in the following equations:



and in order that the carbonic acid may be removed at the same time and so have no interfering action on the formation of di-calcium phosphate, enough lime must likewise be added to combine with the carbon dioxide in the liquid. Thus:



that is, soluble acid calcium phosphate is converted into di-calcium phosphate which, at first, is flocculent and encloses all suspended particles; and subsequently becoming crystalline, particularly in consequence of violent agitation of the liquid, remains attached to the solid particles and rapidly carries them down in sedimentation. After precipitation has been completed the sewage is allowed to flow into sedimentation cisterns or is transferred to Dortmund tanks. If the Dortmund tank with conical bottom is used it should be so proportioned that the upward flow will not exceed 0.02 inch per second. The sludge which settles into the cone may be drawn off from the bottom to the filter press or centrifugal and when partially dried by this means it is sent to cylindrical direct-heat rotary driers, where it is dried to the commercially allowable 10 per cent. of moisture.

But the calcium phosphate does more than carry out the solid suspended matters. It combines by adsorption with the apparently soluble colloidal matter and carries it down as well, wholly or in part, and hence carries down a very large portion of the bacteria, making a clear colorless nearly-bacteria-free effluent. The effluent is in excellent condition for further treatment by sand filtration, intermittent filtration or any of the biological means which have been suggested for the treatment of sewage, raw or settled. The removal of the colloidal matters in addition to the suspended matter so purifies the sewage that generally it may be discharged into any considerable body of water or stream of reasonable volume without deleterious result.

The Dortmund tank offers the advantage that it may be installed upon a smaller area than that consumed by the tanks or cisterns of the septic system, a very important consideration when it is desired to establish a purification or disposal plant

within the confines of a municipality. With the Dortmund tank, or the Machlachlan tank, which is very similar, the treatment of a large body of sewage may be effected in a comparatively small space.

The use of phosphate has this advantage over aluminum or iron salts, that the precipitate of the former does not remain flocculent but becomes crystalline and that sedimentation is thereby promoted and is more prompt and rapid. In addition to this the phosphate precipitate has an agricultural value as plant food which, of course, the aluminum and iron precipitates do not have. Furthermore, the use of an excess of the precipitant, while unwise, can have no deleterious influence upon the agricultural value of the sludge and in case excess is accidentally used the phosphate will be recovered in the sludge and no ultimate loss occasioned. Yet the quantity of phosphate used should be such that the precipitated phosphate should have nearly the same weight as the suspended solids. This is essential to the best results in precipitation and in draining the sludge.

The settled sludge obtained varies in its properties in accordance with the quantity of phosphate used in producing it, and the mode of application of lime to the sewage as well as the completeness with which carbonic acid has been simultaneously precipitated. If the lime be added too rapidly there will be tendency to production of tri-calcium phosphate which will remain permanently flocculent and so interfere with filtration. Furthermore, it is not so readily soluble in the soil and has a somewhat lower agricultural value than the di-calcium phosphate. In the absence of carbonic acid di-calcium phosphate is insoluble in water and all the phosphate used, if care is exercised, may be completely recovered and in form practically as valuable for plant food as the acid calcium phosphate originally employed. In addition to the nitrogen of the suspended matter the phosphate contained therein as well as much of the phosphate contributed to the sewage by urine is secured. It has been found that one million gallons of sewage will return at least half a ton of dry sludge and in some cases more than this. The sludge contains about 1.5 per cent. of nitrogen and depending upon the amount of phosphate used in the precipitation, over twenty per cent. of phosphoric acid. The value of the sludge independent of the amount of phosphate employed will be from four to five dollars per ton on account of the nitrogen recovered, and while the material recovered cannot be expected to cover the cost of recovery or treatment of the crude sewage it contributes materially toward the net cost of disposal. Thus if the cost of disposal, by the septic or biologic process, amounts to five dollars per million gallons which will probably not be considered too high an estimate, the cost of precipitation with the phosphate will not greatly exceed this and the returns from nitrogen recovered will very nearly balance the account. We not only provide here a means for purifying the sewage to the extent that it may be discharged without further treatment into most of the water courses without offense, but the material recovered partly covers the expense of treatment. Besides this we have provided for the conservation of the very important urban waste for use in agriculture.

The process may be equally well applied to the treatment of turbid and colored water supplies. Suspended matter is completely removed, and the coloring matters, particularly when plenty, are coagulated and precipitated furnishing an effluent clear, colorless, and with bacterial content very materially reduced, generally to an extent entirely allowable in good potable water. In addition if the precipitation be affected by sodium carbonate followed by lime the hardening constituents will be simultaneously removed and the water consequently softened.

The process has not yet found extended application but enough has been done with it to prove its availability for the successful treatment of municipal sewage, and the recovery

by means of it of the suspended organic and much of the soluble phosphates present therein.

It is important that the process shall be operated in careful and skilled hands. If carbonic acid is not removed, di-calcium phosphate is not as well precipitated and a considerable loss may be occasioned. If the lime is added too suddenly and in too large quantity at a time the tendency to the formation of tri-calcium phosphate will interfere with prompt and rapid sedimentation and will increase the cost of recovery as well as reduce the value of the sludge.

If too much lime is used, more than is necessary to precipitate the phosphoric acid added and the urine phosphoric acid present, as di-calcium phosphate and carbonic acid as calcium carbonate, making a neutral effluent and sludge, there will be liberation of ammonia with consequent loss of nitrogen and production of offensive odors. If violent agitation is not provided when the lime is being slowly added, crystallization is not so prompt and sedimentation not so rapid.

The sludge, if sufficient phosphate has been used in the precipitation, and proper agitation of the sewage has been applied during precipitation, should be capable of being drained of mechanical or liquid water in a filter press or even upon a gravity filter, and then the character of the sludge is such that it is too viscous and colloidal to admit of successful treatment in the filter press or on the gravity filter, then it may be treated in one of the several centrifugal machines designed for the purpose.

The sludge dried by means of the filter press or the centrifugal may be further dried at very small cost in any one of the direct-heat cylindrical rotary driers, and bagged for storage, transportation and use.

The process is well worthy of the considerate attention of engineers charged with the disposition of the municipal sewages. It would seem a public duty to use every means to conserve the municipal waste caused by the method ordinarily employed for the treatment of sewage. Among the advantages of the process may be named:

1. The precipitation of the suspended matter is complete.
2. The effluent is clear, colorless, and has comparatively low bacterial content.
3. The effluent may be discharged into water courses without further treatment and without serious detriment, particularly if treated with calcium hypochlorite or other disinfecting agent.
4. The organic suspended matter and much if not all of the colloidal matter in the sewage are recovered in condition suitable for use in agriculture.
5. The phosphate employed is recovered in form available directly as plant food, and therefore of as high value as that originally employed. The cost of the phosphate beyond a small mechanical loss in handling and interest upon funds invested in the product may be disregarded.
6. It is probable that much of the phosphoric acid furnished to the sewage by urine will be recovered in the sludge.
7. The net cost of the disposal of sewage will be materially reduced.
8. In this process, sedimentation is more rapid than in ordinary sedimentation processes and may be effected in the Dortmund or Machlachlan tank.
9. The space required for the plant and the expense of constructing the plant are considerably less than like items for septic or biologic plants which are so extensively used. The plant may, therefore, be installed within city limits, where, because of the space required, the other processes named would be wholly impracticable.

The disadvantages of the process, if there are any, will quickly be discovered. Among these may be mentioned:

1. The difficulty of separating the mechanical or liquid water from the sludge. If the lime has been added too rapidly or much colloidal matter is present in the sewage, filtration is slow

2. The necessity for daily care of the sludge and the labor involved in it.

The advantages of the process, however, seem to outweigh the disadvantages by an adequate margin, and the process is, therefore, commended to the favorable consideration of engineers and chemists charged with the disposal of municipal sewage.

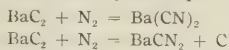
264 RIVERSIDE DRIVE
NEW YORK CITY

MANUFACTURE AND USES OF CYANAMID¹

By E. J. PRANKE

The problem of the fixation of atmospheric nitrogen is one which has engaged the attention of scientists for the greater part of a century. The rapid growth of the fertilizer industry that has attended the development of agricultural science, and the great increase in the number and extent of chemical industries, during the past fifty years, has emphasized the necessity for artificial methods of maintaining and increasing the world's stock of combined nitrogen. One of the influences that stimulated immediate action was the introduction in 1887 by MacArthur and Forest, and at about the same time independently by Siemens and Halske, of Berlin, of the Cyanide Process for leaching gold and silver from their ores. This produced a strong demand for cyanides, which had hitherto been used to the extent of only a few hundred tons a year, principally in the dye industry and to a smaller extent in electroplating.

Attempts had been made early in the nineteenth century to bring about the direct synthesis of cyanogen from atmospheric nitrogen and carbon. Among other processes, that worked out in 1847 by Bunsen and Playfair, in which barium carbonate was heated in an atmosphere of pure nitrogen, seemed promising, but did not prove to be commercially successful. The introduction of the electric furnace in 1894 by Moissan and by Willson, for the production of carbides on a large scale, gave new direction to the researches. Siemens & Halske, among others, adopted it for the working out of the problem of nitrogen fixation. In 1895 they worked on the process of Prof. H. Mehner, which consisted in fusing a mixture of sodium carbonate and carbon and conducting nitrogen through the hot mass. In the same year they took up the process of Prof. Adolph Frank and Dr. Nicodem Caro, which consisted in subjecting a mixture of barium carbide, sodium hydroxide, potassium hydroxide and carbon at a high temperature to the action of steam and nitrogen. Frank and Caro, with the cooperation of F. Rothe, soon learned that dry nitrogen is essential to successful absorption. In 1898 it was found that barium carbide alone, heated to a temperature of 700 to 800° Centigrade, in an atmosphere of nitrogen, readily absorbs nitrogen and forms a product in which about 30 per cent. of the nitrogen is present as barium cyanide and about 70 per cent. as barium cyanamide. The reactions may be represented by the equations:



It was further found that on fusion of this mass with soda the cyanamide is converted to cyanide. This mass can then be leached with water, and the cyanide solution thus obtained can be converted to sodium ferrocyanide, which is easily separated in a pure form, and which can be sold as such or be converted into pure sodium cyanide by fusion with metallic sodium.

The interruption in the production of gold in Africa, due to the Boer war, caused a decline in the price of cyanide, which stimulated the search for cheaper methods of production. It was found that calcium carbide could not only be manufactured at a lower cost, but it had the advantage of a lower molecular weight. With calcium carbide a temperature of from 1100 to 1200° C. is required for absorption, but in this case the nitrogen

is fixed exclusively in the form of calcium cyanamide. On fusion with alkaline salts the cyanamide is readily converted to cyanide, and this can be extracted and purified in the usual manner.

Agricultural experiments with the crude calcium cyanamide showed that this material is suitable for use as a nitrogenous fertilizer, and patents were issued in 1910 to Dr. Albert R. Frank, son of Prof. Adolph Frank, and to Herman Freudenberg, a co-worker of A. R. Frank, protecting the use of Cyanamid for this purpose. The basic patent protecting the process of manufacture of Cyanamid was issued to Prof. Dr. Adolph Frank and Dr. Nicodem Caro in 1908.

The large demands of agriculture for cheap nitrogenous fertilizer materials have directed the efforts of the manufacturers towards the production of Cyanamid rather than of cyanides and other derivatives. At present the total output of sodium cyanide derived from Cyanamid is only about 2000 tons per annum, while the world's production of Cyanamid is estimated at about 120,000 tons per annum.

MANUFACTURE OF CYANAMID

Calcium cyanamide is formed in accordance with the equation



The raw materials, therefore, are calcium carbide and nitrogen. Calcium carbide is formed in accordance with the equation



The raw materials for this reaction, therefore, are lime and coke.

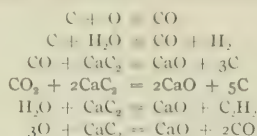
For the production of carbide, lime, from 1 inch to 2½ inches in size, and coke, about ½ inch, are mixed, in the proportions demanded by the equation, to produce a carbide about 80 per cent. pure. The mixture is shoveled continuously into a 3-phase electric furnace. The furnace consists of a supporting base and four retaining brick walls which are filled with the lime and coke mixture, into which is submerged three carbon electrodes carrying the current. The resistance of the materials to the passage of the current raises them to a temperature at which the lime melts freely and combines with the coke to form liquid carbide. At intervals, as the carbide accumulates, it is tapped off through a suitable tapping hole at the side of the furnace into iron cars. After cooling, the carbide is crushed and ground to a fine powder, and is then packed in perforated cylindrical steel cans in the axis of which is a cylindrical paper core. The can with the carbide is set in a brick walled oven, slightly larger than the can, and is covered with an iron lid. A carbon pencil is run through the paper core in the axis of the can. Upon passage of the electric current, the carbide is heated, nitrogen is admitted to the can, and the absorption takes place very readily, raising the temperature to about 1100° to 1200° C., at which point it is maintained until the absorption is complete. The reaction $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$ is exothermic, and the heat given out is almost sufficient to maintain the mass at the combining temperature. Upon completion of the reaction the cans are removed and the product is allowed to cool. It is a bluish black solid, containing small glistening crystals of pure calcium cyanamide.

PREPARATION

The nitrogen required for the manufacture of Cyanamid is separated from the air by either the liquid air process or the copper oxide process. The latter is in use at present by the American Cyanamid Company. The copper oxide process is based upon the ease with which heated copper combines with oxygen. The very finely divided copper suspended in a mass of asbestos or other inert material is contained in boiler shells provided with means for supplying heat externally. Air is pumped through the retort, which is at about 800° C., and is completely deprived of its oxygen. The nitrogen is then freed from carbon dioxide by passage through a caustic soda tower. The moisture

¹ Address before the Nashville Section of the American Chemical Society, November 15, 1912.

is removed by refrigeration, followed by passage of the gas through layers of lime, and finally through calcium chloride. The nitrogen must be pure and dry, since otherwise there is a destruction in the nitrifying ovens of the carbon pencil and of calcium carbide in accordance with the following reactions:



The oxidized copper in the nitrogen separation retorts is reduced in place by reducing gases, such as natural gas.

PREPARATION FOR USE AS A FERTILIZER MATERIAL

The crude Cyanamid obtained from the nitrifying ovens, after cooling, is crushed to a fine powder, and is passed into rotating, slightly inclined, steel cylinders, in which it is treated with sufficient water to eliminate the carbide and to slake the calcium oxide. A further slight addition of water is made before the material is run through briquetting machines.

The resulting bricks harden rapidly and are stored until they can be crushed just prior to shipment. Crushing is done in a series of rolls with intermediate screens, the final product having a coarseness of about 15- to 50-mesh screens. It is packed in ordinary fertilizer bags and distributed in carload lots to manufacturers of mixed fertilizers. The material so prepared contains nitrogen equivalent to about 19 per cent. ammonia.

It analyses approximately as follows:

Calcium Cyanamide	45%	Iron and Alumina	2%
Calcium Carbonate	4%	Silica	2%
Calcium Hydroxide	27%	Combined water	4%
Calcium Sulphide	1%	Free moisture	1%
Free Carbon	14%		

USES OF CYANAMID

At present, Cyanamid is used in this country principally for agricultural purposes. It is known to have a fertilizing value equal or superior to that of other common products used for the same purpose. Some of the earlier experiments with this material indicated an uncertain action on very acid moor soils, but the same thing is true of other fertilizers requiring nitrification prior to absorption by the plant, and is the fault of the soil and not of the fertilizer. Such soils must be restored to normal condition before fertilizers can be expected to have their full effect. In other cases, experimenters applied quantities far in excess of those used in practical agriculture, and obtained a lower efficiency of utilization than with the normal applications. As a general conclusion from the hundreds of recorded experiments and from the testimony of practical agriculturists, it may be said that when Cyanamid is used in the same way as other fertilizers are used in ordinary practice, its efficiency of utilization is about the same as that of the high-grade fertilizer materials, and superior to that of the low-grade fertilizer materials.

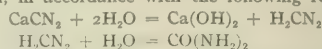
The particular advantage of Cyanamid as a fertilizer material lies in the advantageous effects that follow its admixture with other constituents of complete fertilizers. It greatly improves the mechanical condition of such mixtures, and by its alkaline properties prevents the escape of valuable nitrogen oxides and of bag-rotting hydrochloric acid, set free by the action of free acids in acid phosphate upon nitrates and chlorides in the mixtures.

Statements have been made that there is a loss of ammonia from Cyanamid during long-continued storage. It has been found, indeed, that the nitrogen percentage in stored material does decrease, especially in very damp climates, but it has been determined by very careful experiments both on a small scale and on a large scale in fertilizer factories, that such decrease in

the nitrogen percentage is due not to any actual loss of nitrogen, but to the increase in the weight of the material, due to its absorption of carbon dioxide and of moisture from the atmosphere. Part of the moisture absorbed is fixed chemically into forms from which it is not recovered on heating in a drying oven, hence it is necessary, when testing the storing qualities of this fertilizer, to weigh the material before and after the period of exposure and to determine the nitrogen percentage each time.

SOIL ACTION OF CYANAMID

It has been definitely established by the researches of Ulpiani and Kappen, among others, that cyanamid applied to the soil is completely converted in the course of a few days into urea, by the catalytic action of the colloids and other constituents of the soil, in accordance with the following reactions:



The urea is further converted by bacterial action and possibly by chemical processes into ammonia, which further reacts with zeolites, humates, and other soil constituents, to form double ammonium salts, that are retained as a part of the soil, until further bacterial action or the solvent effect of plant roots makes them available to vegetation. Cyanamid is said to be completely utilized by the crop in from 60 to 80 days.

OTHER USES

When Cyanamid is subjected to the action of superheated steam under pressure of several atmospheres, it is converted almost quantitatively into ammonia and calcium hydroxide. It thus serves as a convenient and cheap source of pure ammonia. By the Ostwald process, which uses thoria and ceria as catalytic agents, ammonia can be commercially converted into nitric acid.

By fusion of Cyanamid with alkaline salts in the presence of carbon, cyanides are easily produced and can be separated and purified as desired.

When Cyanamid is extracted with water between 70° and 100° C., nearly all of the nitrogen is converted into dicyandiamide (H_2CN_2)₂. This compound is used in the dye industry and also in the explosives industry in place of ammonium oxalate to reduce the temperature of the explosive gases.

Other derivatives, such as urea, guanidin and its salts, and various dicyandiamidin salts are now being manufactured in Germany. One or both of the hydrogen atoms in the amide group in cyanamide, $CN.NH_2$, can be replaced by metals, alkyl or aryl groups, alcohol groups, aldehyde groups, and others, thus leading to an immense number of organic derivatives. The possibilities in this field have been investigated but little.

Various compounds of Cyanamid, and its derivatives, with alkaline salts and carbonaceous materials, are made and sold in Germany under the names of Ferodur, Intensit, Hesselin, and others. These compounds, known as "hardening" or "cementing" powders, are used in place of cyanides, ferrocyanides, waste leather and similar materials, for case-hardening of steels. These products containing Cyanamid are not only cheap but they are efficient for the purposes for which they are intended.

FUTURE OF CYANAMID INDUSTRY

The Cyanamid industry is undoubtedly only in its infancy. At present there are four factories in Germany, four in Italy, two in France, and one each in Austria, Norway, Sweden, Switzerland, Japan, and America. The American Cyanamid Company built its first plant at Niagara Falls, Ontario, in 1909, beginning commercial manufacturing January 1st, 1910. Additions to the plant, which will be completed in March, 1913, will give a capacity of 25,000 tons per annum, and by the end of the year the full productive capacity of the company, including the extensions now under way, should be 50,000 tons per annum.

NASHVILLE, TENN.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

UNITED STATES STATISTICS FOR 1912

Number 2 of Volume 95 of *The Engineering and Mining Journal* contains a comprehensive treatment of many of the minor and major minerals and metals, giving statistics of production for 1912, and reviewing progress in various departments of metallurgy. An abstract of this entire number follows.

PRODUCTION OF METALS IN THE UNITED STATES IN 1912

METAL	UNIT	PRODUCTION
Copper ¹	Pounds	1,242,836,024
Ferromanganese	Long tons	202,186
Gold ²	Dollars	91,685,168
Iron	Long tons	29,445,068
Lead ³	Short tons	418,224
Nickel ⁴	Pounds	33,311,233
Mercury	Flasks (75 pounds)	25,147 ⁵
Silver ²	Troy ounces	62,369,901
Zinc ⁵	Short tons	347,922

¹ From ore originating in the U. S.

² Preliminary statistics reported by Director of Mint.

³ Refined lead from ore and scrap originating in the U. S. Antimonial lead included.

⁴ Imports for first 10 months of 1912. This nickel is refined in the U. S. for the production of metal, oxide, and salts.

⁵ Reported by U. S. Geological Survey.

⁶ Total production of smelters, except those treating dross and junk exclusively; includes spelter derived from imported ore.

MINERAL AND CHEMICAL PRODUCTION OF THE UNITED STATES IN 1912

SUBSTANCE	UNIT	PRODUCTION
Arsenic	Pounds	5,852,000
Coal, anthracite ⁹	Short tons	511,964,403
Coal, bituminous ¹	Short tons	427,655,966
Coke ¹	Short tons	41,803,199
Copper sulfate	Pounds	39,480,741
Iron ore	Long tons	59,485,477
Petroleum	Barrels (42 gallons)	218,970,815
Tungsten ore	Short tons	1,290 ²

¹ Estimates of Coal Age.

² Reported by U. S. Geological Survey.

METAL PRODUCTION OF THE WORLD IN 1912

METAL	UNIT	PRODUCTION
Gold ¹	Dollars	469,618,083
Silver ²	Fine ounces	229,569,903
Copper ³	Metric tons	1,004,844
Tin ⁴	Long tons	114,196
Platinum ⁵	Ounces	322,000

¹ The Transvaal furnished 40.1 per cent. of the total, the United States supplied 19.5 per cent., and Australasia 12.1 per cent.

² London continues to be the chief silver market of the world. Mexico is the largest producer, having contributed 76,500,000 fine ounces in 1912; the production of Canada was 35,250,000 fine ounces in 1912.

³ Figures are based upon crude copper, i. e., the smelters' production. The United States supplies over half of the world's production.

⁴ The visible stocks of tin on December 31, 1912, were reported to be 10,977 long tons. The average price during the year was 46.096 cents per pound as against 42.281 cents in 1911.

⁵ Includes productions of Russia (310,000 ounces) and Colombia (12,000 ounces). Small quantities are also obtained in British Columbia and Australia, but the amount is unimportant.

There were 60,178,477 tons of iron ore consumed in the United States in 1912, and the production of pig iron amounted to 29,647,274 tons. The following table shows the production for 1912 classified according to the uses for which it was intended:

Foundry and forge.....	5,965,591
Bessemer.....	11,740,055
Basic.....	11,386,176
Charcoal.....	353,266
Spiegel and Ferro.....	202,186

Total..... 29,647,274 tons

The sulfur industry in 1912 was marked by new activities

in exploration. The Union Sulfur Co. produced in 1912 more sulfur than the entire world consumed. No Sicilian crude was imported in 1912, although a few thousand tons of refined sulfur came from that source, and probably about the normal amount was imported from Japan at Pacific ports. A quiet year was experienced by the importers of pyrites; the domestic mines supplied about 300,000 tons, or less than 25 per cent. of the normal consumption of the United States, but, due to the over-extension of the phosphate industry in 1911, the 1912 demand was light.

THE CHEMICAL ACTIVITIES OF BELGIUM

There are 10 zinc works, producing 48,450 metric tons of finished zinc, and 13 zinc foundries, producing 198,230 metric tons of rough zinc, in operation in Belgium. In the Province of Hainaut there were 2,057 coke ovens in operation in 1911, consuming 2,698,480 metric tons of coal. Other statistics for 1911 follow:

PRODUCT	IMPORTS	EXPORTS
Chemical products	\$24,646,197	\$14,587,631
Window glass	75,576	7,163,165
Plate glass	49,022	5,643,952
Iron and steel	18,332,894	1,624,562

THE INCREASED USE OF CHARCOAL IRON

Some very good work (A. I. Findley, *The Foundry*, 40, 534) has been done recently in the direction of giving charcoal iron a larger place in car wheel and special mixtures. There have been some results, and the demand upon the railroads for freight car wheels which will better stand the heavy service of recent years is assisting the movement. However, cost is so controlling an influence in railroad buying that the low level of coke pig iron has held down the charcoal product, and much is yet to be done to secure recognition for it on the score of quality. In chilled work and for castings requiring a special selection of raw material, charcoal iron is making headway, and the outlook has been sufficiently promising to encourage some additions to the capacity of Michigan charcoal furnaces in the past three years. Lately, Mayari pig iron, which owes its properties to a small content of nickel and chromium, has been offered as a component of chilled roll mixtures and for castings requiring special strength.

A new process for making charcoal wrought iron is being operated by a works near Philadelphia, Pa. An open hearth furnace is used; it is first heated by oil or gas, and then a layer of charcoal is spread on the hearth and the charge of pig iron is placed on top of it. The iron is covered with a layer of charcoal, then cold air from tuyères burns the charcoal, melts and boils the iron in the customary manner. The fused metal runs through the lower layer of charcoal, and more charcoal is added as required. The impurities are oxidized by the usual cold blast. The product is said to have high purity.—W. A. H.

GILLED TUBING

"Sauerbier" patent spiral-gilled tubing for heating, drying and refrigerating plants is being manufactured in Germany from seamless Siemens-Martin steel tubes with corrugated spiral gills, the whole being galvanized. It is claimed that this tubing has a large heating surface combined with great strength.

THE TOXICITY OF WHITE LEAD

Line (*Drugs, Oils and Paints*, 28, 255) reports that a large decrease in plumbism in the manufacture of white lead has followed the abolition of female labor and youthful labor in England. The decrease is also consequent on ventilation, the

use of respirators, overalls, enforced cleanliness, and the avoidance of lead dust. No material increase in the cost of manufacture has resulted, but death and suffering have been averted. Plumbism is usually easy to diagnose, yet lead occasionally induces obscure affections of the nervous system, the cause and true nature of which are not always recognized. The grinding of white lead with oil was formerly a large source of lead poisoning, because the pigment was dry, and consequently the grinding mill attendants and the lead work laborers inhaled lead carbonate dust; but since in many factories the paint is now made with the lead carbonate in the moist state, by gradually displacing the moisture with oil during the process of grinding, this source of danger has decreased. There is said to be more danger in the process of grinding basic lead sulfate into paint oil than there is when grinding the moist lead carbonate in oil. Line emphasizes the dangers incidental to the manufacture of red lead, these being referred to as "terrible."

TANTALUM AS A SUBSTITUTE FOR PLATINUM

In a paper on "Tantalum Electrodes," published in the *Chemiker-Zeitung*, 36, No. 126, 1233, O. Brunck discusses the substitutes for platinum and the employment of tantalum as a partial substitute for this costly yet valuable metal.

As there is little prospect that the price of platinum will ever decline to any considerable extent, science and industry have made strenuous efforts to obtain a substitute. Quartz glass at a moderate price offers, for certain purposes, a substitute for platinum, although not quite its equivalent. It is resistant to acids, with the exception of hydrofluoric acid, and is insensible to sudden changes of temperature, but it is breakable and is a poor conductor of heat. Chemical apparatus has also been made of an alloy of 90 per cent. gold and 10 per cent. platinum; this alloy is harder and tougher than gold, but is, unfortunately, more difficult to work than either one of the component metals. It is likely that it might replace platinum entirely if its melting-point were higher; as it is, its scope of application is large enough, but the economy attained is small, for the price of apparatus constructed of it amounts to about two-thirds of that of platinum, owing to the higher cost of molding.

A German concern has recently proposed tantalum, originally intended only for the manufacture of metal filaments for electric incandescent lamps, as a partial substitute for platinum, and has put on the market various forms of apparatus and instruments made out of that metal at a price of \$0.625 per gram, including cost of molding. As a material for surgical and dental instruments tantalum has already found favor with practitioners; but in chemical laboratories, tantalum dishes are, so far, the only form in which the metal is employed. Brunck states that the sensibility of tantalum to oxygen at the higher temperatures and to hydrofluoric acid prohibits a more general use of the metal as a platinum substitute. In a vacuum tantalum will stand the highest white heat, but, heated in the air, it commences to oxidize below a red heat; and while it is perfectly resistant to water solutions of alkalis, the compact metal is destroyed by fused alkalis.

Experiments conducted by Brunck showed that tantalum could be substituted for platinum as cathode material without reserve, while this was not the case with regard to anodes. He found, however, that if it was desired to use tantalum as anode material and to work with a tantalum cathode and a platinum anode, the tantalum anode might be plated with a thin layer of platinum which could be easily accomplished electrolytically. A coating of a few centigrams of platinum was found to suffice. It was found to be even better to employ an anode of tantalum wire which was plated with platinum by a process patented by Siemens and Halske. Brunck reports that tantalum has even some advantages over platinum as cathode material; for example, zinc and cadmium show no dis-

position to enter into an alloy with tantalum on its surface, hence there is no need of the cathode being plated with copper or silver as in the case of a platinum cathode. The insensibility of tantalum to *aqua regia* permits the removal of platinum and gold precipitate by that acid. A further advantage of tantalum over platinum is its greater strength and rigidity which prevents the electrodes from getting out of shape by bending. The difference in price is noteworthy, that of tantalum being 40 per cent. less than that of platinum. There is also a saving in weight of about 30 per cent. Brunck considers that tantalum may serve as a substitute for platinum in the different types of bleaching electrolyses.

SULFUR IN ILLUMINATING GAS

L. J. Willien (*Gas Age*, 31, No. 1, 5) points out that in a plant, where both coal gas and carburetted water gas are manufactured, a high percentage of sulfur in the coal has a twofold, and possibly threefold, evil effect, namely: (1) In almost every case a high sulfur content of the gas will be found, both in hydrogen sulfide and carbon disulfide; (2) When the coke is used in the generator of a water gas machine, about 50 per cent. of the sulfur in the coke goes into the gas, so that the sulfur which is not given off in the coal gas will be given off in the water gas; (3) A coal containing a high percentage of sulfur usually contains a high percentage of iron, which will cause clinkering trouble when the coke is used in making water gas. By knowing the percentage of sulfur in a coal or coke, the amount of sulfur compounds that the unpurified gas will contain can be approximately estimated in the following manner: With coal gas, multiply the percentage of sulfur by 20 and the product will be grains per 100 cubic feet of sulfur compounds in the unpurified gas. With water gas, multiply the percentage of sulfur in the coke by 10 and the product will represent grains of sulfur compounds per 100 cubic feet.

In using lime for removing carbon disulfide, while it is necessary to remove the carbon dioxide from the gas, still it is not economical to remove carbon dioxide by passing through a lime box. With six purifying boxes connected so that they can be used in any combination, the most economical method of operation is to fill four of them with oxide and two with fresh lime; allow the crude gas to pass through one of the fresh lime boxes for 24 hours to partially sulfide the lime; have the gas pass through two oxide boxes first, in order to remove hydrogen sulfide, then through the fresh lime to eliminate carbon dioxide, then through the lime box containing partially sulfided lime to remove carbon disulfide, and finally pass through one of the other two boxes filled with oxide, keeping one oxide box in readiness to be cut in when necessary. Where the amount of sulfur compounds allowed in the gas is limited to 30 grains per 100 cubic feet, it is hardly safe to use a coal containing more than 2 per cent. of sulfur and keep within the limit by using lime. Where the limit is 20 grains, the coal used should not contain more than 1.5 per cent. of sulfur.

THE USE OF GASES FOR FIRE EXTINCTION ON BOARD SHIP

A discussion on the use of gases for fire-extinction and fumigation on board ship took place at the meeting of the British Institute of Marine Engineers on November 25, 1912. A report of such parts of this as are of interest to the chemical engineer is presented below.

G. Canning said he thought that the practice of blowing steam into the cargo could be regarded only as a check to initial outbreaks. It had been said that the danger to human beings of systems in which odorless gases were used, could be overcome by impregnating the gas, but such a procedure depended a great deal upon the operator. Canning considered that the possibility of a deposit taking place in the pipes was more likely

in the case of flue gas than in the sulfur dioxide apparatus. In his opinion, sulfur dioxide was also more efficacious for fumigation purposes.

P. Selow said that with the carbon dioxide system ten cylinders, each of 40 pounds of liquefied gas, would be sufficient to deal with a space of about 42,000 cubic feet. The average number of cylinders supplied to a vessel was 50, and the cost of a new installation should not be more than \$1750.00 at the outside.

Prof. Armstrong said that carbon dioxide, sulfur dioxide, steam, and flue gas systems were all based upon the same principle—the reduction of oxygen in the air. The carbon dioxide system required a somewhat expensive equipment of iron cylinders filled with the compressed gas, and there was the disadvantage that when the supply was exhausted, as it might be on a long voyage, the system would be valueless. The same difficulty occurred in the case of the sulfur dioxide system, with the additional objection that the use of sulfur dioxide would injuriously affect the metal-work of the ship and certain cargoes. Steam had the advantage that it was always there as long as the boilers were at work. The flue gas system also had that advantage and was very ingenious, as it utilized a waste material, which could be obtained as long as the coal supply lasted, and which had practically the same power as the other gases of acting as an extinctive agent, while it was without their deleterious effect on the cargo.

J. Craig stated that the temperature of the flue gas was reduced to about 100° F. when put into the cargo. There was, he maintained, no deposit in the pipes with this system. He pointed out that a cooling process was necessary in fire extinction.

K. Scott considered the use of inert gases as of particular value for the prevention of spontaneous combustion in cargoes of coal, cotton and wool. He called attention to the fact that a distinctive odor could be imparted to inert gases by the addition of carbon disulfide, mustard oil, etc., and that the fumigating power might be thus increased.

A NEW TIMBER PRESERVING PROCESS

In the process for the preservation of timber devised by R. A. Marr, the preservative material is melted paraffin with silica in suspension, together with a small amount of naphthalene. The silica used is diatomaceous earth of which 92 per cent. will pass 200 meshes to the linear inch. It is said (*Eng. Min. J.*, 94, 1125) that wood can be permeated to the center, regardless of the dimensions of the timber, in a maximum of four hours as against 12 to 24 hours for creosoting. It is claimed that the treatment will prevent checking, adds resilience to the timber, and renders it immune to the attacks of the teredo and other marine borers, owing to the hardness of the silica. It is also claimed that the treatment is successful with white oak and other hard woods which are impenetrable by other processes. The process is an open-tank one, the experimental plant consisting of a vertical cylindrical tank just large enough to admit a railroad tie and jacketed to retain the heat supplied by a gasoline burner beneath the tank. The tank holds about 125 pounds of the preservative mixture, which costs about \$0.03 per pound. For complete impregnation of oak and pine it requires about 1.65 to 2.00 pounds of solution per cubic foot of timber. Spikes and nails are said to hold better than in creosoted or in untreated wood, and not to rust; and the treated wood does not become waterlogged under any conditions of use.

THE BILLITER ALKALI-CHLORINE CELLS

Allmand (*Chem. News*, 106, 291) reports that J. Billiter, of the University of Vienna, has designed two successful types of non-mercury alkali-chlorine cells. The Billiter-Siemens cell has already been described in several places. It has diaphragms, these being placed horizontally instead of vertically, as is gener-

ally the case. The floor space required is greater, but the diaphragms are stabler chemically and the current efficiencies are high. Several installations of this cell are working on the Continent and in America. The Billiter-Leykam cell is a modified bell-jar cell. The cathodes are, however, arranged underneath the bell-jar, being contained in porous asbestos hoods to catch the hydrogen. The brine leaving the cell does not therefore change the direction of its motion before reaching the cathodes. A far more uniform flow is thus obtained, and the current efficiency is high in result thereof. It is said that the porous asbestos hoods offer very little resistance to the passage of the current. The cell, being furthermore heated by means of hot liquids flowing through earthenware pipes, requires low voltage. At 85°, 12 to 13 per cent. of sodium hydroxide can be made at 92 per cent. current efficiency, employing 3.1 volts. Attendance charges are low and unpurified brine is used. The first installation at Gratwein, Austria, is said to work very satisfactorily.

WATER PURIFICATION IN THE INDUSTRIES

In *The Chemical Trade Journal*, Royal-Dawson states that the best way to keep a boiler as free as possible from sediment is by forcing air through it and greasing the inside with petroleum. A good way is to add petroleum to the water, and this directly avoids the formation of scale. Heavier oils are not to be recommended, as they tend to form fatty acids on dissociation at the high temperature and pressure at which boilers are worked. Fatty acids form a thick coat on the sides of the plant, and in time corrode the metal.

The general method is to use a mixture of soda and lime. The soda precipitates the lime salts as insoluble carbonate of lime, and the lime in a slaked form, or lime water, decomposes the bicarbonates. If the water be heated it can be purified by soda alone, when calcium sulfate is precipitated and the bicarbonates are decomposed by the heat. It is the custom to purify feed waters before they enter the boiler, and only such water as is clear and free from sediment should be used. If such treatment of boiler feed waters were systematically done, and put under proper continual chemical control, the cost of fuel for heating would be greatly lessened, and the life of a boiler would be no anxiety to the chemical engineer.

It is a good recommendation that the works chemist should include in his daily routine of ordinary tests outside the laboratory that of testing the water in boilers for acidity or alkalinity, and have a certain standard to go by.

With regard to trade effluents, the same author goes on to say: The drainage from breweries varies considerably, but it chiefly comes from the 'coppers,' or boiling vats, consisting of hop refuse and soluble nitrogen compounds. The water hardly requires chemical treatment, being so dilute, but in case of necessity a mixture of lime and alumina is recommended.

"Pyrites pits waste contains ferrous sulfate and sulfuric acid in the drainage water. By treatment with oxide of lime, crude gypsum could be obtained in the usual way.

"The refuse water from tanneries contains decomposed animal matter. Sulfide of lime, and arsenic from the use of sheep dips, may also be found. In this case clarification with lime and sulfate of iron, and filtration afterwards, is to be recommended.

"The refuse of the Leblanc soda process, when dried, could either be used as a manure or worked up into other products. The waste effluents from the ammonia soda process contains much calcium and sodium chloride, and from these constituents hydrochloric acid and free chlorine can be produced."

THE SLATE-BED TREATMENT OF SEWAGE

At the Ordinary Meeting of the London Section of the Society of Chemical Industry, on December 2, 1912, W. J. Dibdin gave an account of the success of the slate-bed process. The introduction of this process marks the utilization of one waste product,

slate debris, to effect the conversion of offensive organic waste into an inoffensive earthy form having some manurial value. The action of the slate beds are summarized as follows: The solid matters in the sewage are allowed to settle on shelves of slate supported by slate blocks at a distance of about two inches, these being superposed to a depth of one to five or six feet as required. In consequence of the alternate filling and emptying and resting empty, the deposit becomes the home of many types of organisms that digest the matters and render them inoffensive in like manner to the action by which earthworms produce a humus from organic debris, and throw it to the surface in the form of worm-casts. In the slate-bed the deposit of earthy matter thus formed on the surface of the layer of mud on the slates is washed off by the receding effluent when the bed is emptied, and forms a black slurry, consisting of mineral and indigestible matter with numerous organisms from the bed. This slurry is then placed on a suitable drainage bed for the water to drain off and to allow time for the full digestion of any crude material that may have come from the bed, and, finally, to allow the host of infusoria gradually to extinguish themselves by the natural process of the "survival of the fittest." As a result of experiments during a period of eighteen months at High Wycombe, England, it was found that the quantity of residual matter was equal to only 3.4 tons of 90 per cent. moisture per million gallons of normal sewage. "On the assumption that farmers will remove the air-dried humus at their own cost, the capitalized annual economy will repay the cost of the slate-beds." The nuisance of sludge disposal is also abolished.

THE MANUFACTURE OF SWEDISH FILTER PAPER

Fornstedt (*Paper*, 10, No. 3, 17) describes the processes involved in the manufacture of filter paper in Sweden.

Machine-made filter paper is used chiefly in the household and for technical purposes, while hand-made filter paper for scientific analyses is of better quality, though of different grades and make, according to the character of the analysis to be made. The paper being more or less quick-filtering it is made with regard to whether a mere purification of the liquid is intended or whether the substances collected on the paper are to be qualitatively or quantitatively determined.

Some qualities of filter paper, as white and gray woolen paper, are made generally in small paper mills which are not equipped with steam boilers. The rag is furnished "raw" in the beaters and beaten free, but care is taken to avoid lumps. The paper is made on a cylinder machine and taken wet on the hasp from where it is cut by hand and hung up for drying. A rough mottled surface is produced by means of a coarse wire cylinder running on the wet paper web, the impression remaining very plainly after the paper is air-dried.

The cleanest rag is used for filter paper, and it must be of the best quality and sorted carefully. Iron is, of course, one of the worst impurities in a filtering paper. The rag is boiled with sodium hydroxide, as it gives a lower percentage of ash than lime; and for bleaching a mixture of manganese dioxide (8 parts), sodium chloride (6 parts), and sulfuric acid (5 parts) is used in lead retorts. After the rag is boiled, washed and beaten to halfstuff, it is dried in a centrifugal drier and spread in layers on wooden poles in the bleaching chamber. This chamber is of concrete, lined with wood. After the bleaching chamber is filled with halfstuff, the door is closed and chlorine is admitted through an aperture in the roof. After all air has been expelled, the chamber is well sealed, and the halfstuff, after absorbing the chlorine for several hours, is effectively bleached. Liquefied chlorine is now used in some mills in this bleaching process.

The analysis of boiled and bleached halfstuff shows the following ash percentages (silica and lime):

New shirt cuttings, No. 1.....	0.039
Old linen, white.....	0.132
Old linen, gray.....	0.140
Colored cottons.....	0.177
White cottons.....	0.107
Sulite, bleached.....	0.298
Soda, bleached.....	0.4

It is, of course, a matter of great importance that the water used in the manufacture of filter paper should be as pure as possible, but it is impossible to avoid some ash-containing matter from being introduced to the halfstuff with the water of manufacture and in the transportation of the halfstuff and the process of drying. Generally the increase is from 0.02 to 0.05 per cent., depending on the state of the weather and the condition of the water.

The time consumed in beating varies according to the nature of the material. Halfstuff freshly bleached requires a longer time than that which has been stored some time. Neither too free nor too slow stuff should be used for filter paper. Stuff that is too slow retards filtration—meaning the time taken for a given quantity of water of a certain temperature to filter through a paper of specific diameter. Paper made of too free stuff fails to keep back the finer grained sediments, such as sulfate of barium, etc.

Among the considerations to keep in mind in the manufacture of filter paper are the rate of filtration demanded, the ash content, resistance to sulfate of barium, fine holes, weight, and impurities.

To produce a filter paper of low-ash percentage requires treatment with hydrochloric or hydrofluoric acid or a mixture of these acids, which will remove impurities like ferric oxide, alumina, lime, magnesia and silica, and paper so treated is practically a pure cellulose paper. With hydrofluoric acid silica is removed, and with hydrochloric acid the other substances enumerated are dissolved away. After treatment with acids the paper should be thoroughly washed with distilled water to remove the last traces of acidity.

To test the neutral reaction of the paper after washing, a solution of nitrate of silver is used to advantage. The wet paper is squeezed with the hand over a glass funnel and the water filtered into a test tube. In another test tube containing distilled water a few drops of test solution of nitrate of silver are added, and the same quantity is added to the water expressed from the washed filter paper. The two tubes are then compared against a black background. If not neutral the water from the filter paper will show an opalescence due to the chlorides remaining in the paper, and further washing is necessary. After this treatment the paper is pressed and hung out in open barns in order to freeze it.

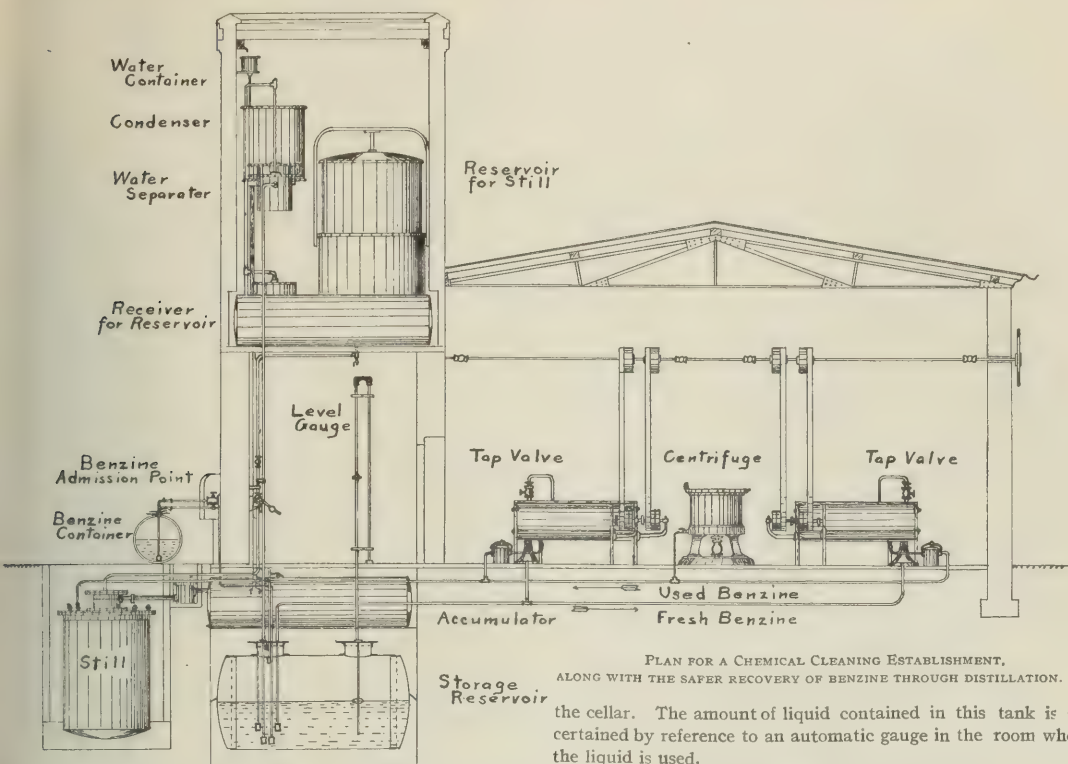
By freezing, the paper is made soft and porous, since the ice crystals formed in it serve to drive the fibers apart. Because of this the finest qualities of filter paper only can be made in the winter time in cold countries.

Experiments have been tried of subjecting paper that has been dried in a warm atmosphere to a subsequent freezing operation in order to impart the desired softness and porosity, but it has been found that paper treated in this way does not become soft and it never comes up to the standard of the best Swedish filter paper.

THE MINIMIZATION OF FIRE RISKS IN THE CASE OF INFLAMMABLE LIQUIDS

A Berlin firm is manufacturing plants for minimizing and preventing risks from fire or explosions in industries where inflammable or explosive liquids are employed.

The inflammable liquid, for instance, benzine, flows out of the tap, as desired, under the normal pressure of protecting gases. The pipes and valves are protected against injury, and the taps



PLAN FOR A CHEMICAL CLEANING ESTABLISHMENT,
ALONG WITH THE SAFER RECOVERY OF BENZINE THROUGH DISTILLATION.

the cellar. The amount of liquid contained in this tank is ascertained by reference to an automatic gauge in the room where the liquid is used.

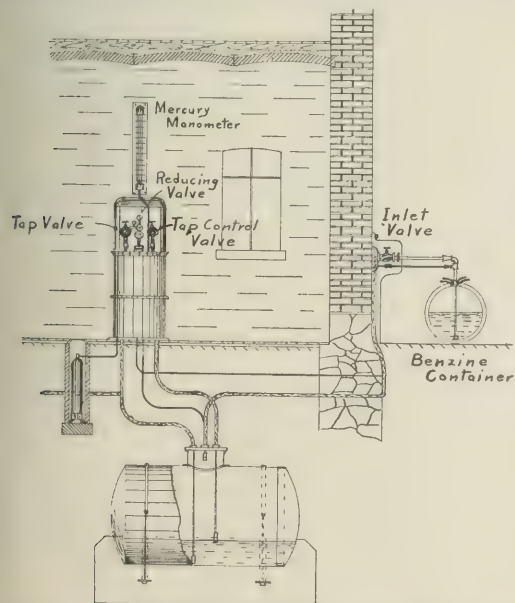
THE BRITISH STARCH INDUSTRY

The cornstarch industry of America has been dealt with in several papers published in the *Journal of the Society of Chemical Industry* (see *Ibid.*, 1900, 617; 1902, 4; 1909, 343; and 1910, 527), but the starch industry of Great Britain has just recently been discussed by Traquair (*Idem.*, 31, No. 21, 1016).

The maize starch industry is centered in Paisley, Scotland, rice starch manufacture is located in England, while Ireland produces the whole of the wheat starch. At one time there were some 10 plants manufacturing maize starch in Paisley and neighborhood; at present there are 5. These grind about 600 tons of Indian corn weekly and produce about 20,000 tons of starch and corn flour annually. The process of manufacture is practically identical with that employed in America.

Traquair states that the future development of the maize starch industry seems to lie along the line of (1) technical utilization of the maize glutens; (2) the application of diastatic conversion to the production of starch sugar in a concentrated solution; and (3) new acid conversion methods and products. The peculiarity of the British position is that the corn is all imported and shows a wide diversity of quality and origin. This state of affairs calls for some flexibility in the process to enable the best results to be obtained.

The present position of the industry is said to be a precarious one. The import of American maize starch exceeds the home production, and represents the surplus of the enormous production of the United States; it is frequently sold at a price which hardly covers the cost of production. This policy has resulted in the closing of the smaller starch works and has forced the others to go in for special products and treat American pearl starch more as a raw material than a manufactured article. The total export of maize starch from America in 1911 was 37,430 tons, of which 92 per cent. went to Great Britain.



CROSS-SECTION OF AN AUTOMOBILE GARAGE PROVIDED WITH SAFETY DEVICES FOR MINIMIZING RISK FROM FIRE
The same scheme may be applied to industries wherein benzine is used

The raw material of the rice starch industry is broken rice, and from a chemical point of view the process is simply the solution and separation of the proteids and fiber by treatment with a weak alkaline solution. Rice starch is said to be unequalled as a cold water laundry starch, as it easily penetrates the fabric, owing to its very small granule and is swollen during the ironing process. There are 10 to 12 plants in operation, but only 3 or 4 of these are large.

Wheat starch is the best starch for linen dressing and finishing, and the location of two plants in the north of Ireland follows the natural course. The raw material in the modern process is wheat flour, and the gluten is recovered instead of being lost as in the old fermentation process.

THE SULFITE WASTE LIQUOR PROBLEM

In THIS JOURNAL (5, 78-9) is published some correspondence relating to the utilization of the waste liquors of sulfite cellulose mills which recently appeared in several German journals. It is of interest to again note that the controversy is still in progress in the columns of our foreign contemporaries in regard to the practical and economical utilization of the waste liquors from the sulfite cellulose process, and the author of an article in *Papier Zeitung*, which a later correspondent criticized, comes to the defense of his paper in a recent issue of that publication, in a communication that forms an addition to the literature of the subject. He says, in part, according to *Papier*:

"In no respect is the article in question directed against the utilization of sulfite waste liquors; on the other hand a possibly profitable process is heartily recommended to cellulose manufacturers. But when a daily paper of the importance of the *Frankfurter Zeitung* publishes inadequately verified technical articles, there is danger that cellulose manufacturers or capitalists may be tempted to invest money fruitlessly in waste liquor utilizations. And there should particularly be a warning against the production of products of low value that afford no promise of interest on capital.

"Such, however, is notably the process of coal briquetting with unpurified waste liquor, rich in ash, which is commended in the *Frankfurter Zeitung*. There is no significance in the fact that Privy Mining Councilor Francke has written on the subject in 1910; rather this is proof of the slight extent to which the value of the experiences described has been recognized. Even the *Frankfurter Zeitung* is as yet unfamiliar with the failures that have been encountered in the employment of unpurified sulfite waste liquors and cellulose pitch in coal briquetting. Neither neutral concentrated cellulose pitch nor acid concentrated waste liquor furnish unobjectionable briquettes; only purified, consequently to a certain extent ashless, liquor could be employed for coal briquetting. Almost all the large German banks have had propositions for coal briquetting with sulfite waste liquors submitted to them and the unanimous opinion of experts has been to the effect that the briquettes were of low value or unfit for use."

How waste liquors could be freed from acid or purified, it was not the purport of this paper to discuss, the author continues; it was intended only to warn against extravagant expectations, for, until to-day, the commercial value of sulfite briquettes has been nowhere proven. In cellulose manufacturing circles so far, the more rational decision has been arrived at to profit by the failures of others before throwing away money on undertakings devoid of prospect.

Against ore-briquetting with sulfite waste liquors nothing is said, only the fact is noted that the few furnaces that have so far used the process, have kept their experience secret and that, for this purpose, license-free concentrated sulfite waste liquors can be used just as well as patented, solid cellulose pitch. "If the agriculturist wishes to obtain lime for fertilizing pur-

poses, he can do so cheaper by methods other than the use of sulfite waste liquors, the product of which, under the most favorable circumstances, is gypsum. Agricultural expert authorities are, however, uttering earnest warnings against the overplastering of the soil (by means of superphosphate, for instance). The organic nutritive substances of the sulfite waste liquors, which are always of value to plant life, have not hitherto been furnished to the farmer in their best available form. Least of all are cellulose pitch or concentrated liquor adapted for this purpose, for their hygroscopic properties and their crust-forming tendency are serious disadvantages, apart from the fact that the material is much too expensive for the farmer. If sulfite waste liquors are to be utilized in agriculture, unobjectionable products must first be obtained from them. The advertisement of sulfite-waste liquor that has been concentrated by any means is no assistance.

"Against the possibility of 'donating' sulfite waste liquors for road sprinkling, there is no objection to be made. But in the *Frankfurter Zeitung* there is no mention made of 'donating,' rather the millions to be earned in Germany by concentrating plants was enlarged on. For this reason, to prevent misunderstanding, the fact was mentioned, that the cities, in spite of exhaustive tests, would have nothing to do with waste-sulfite liquor for road sprinkling. They prefer to use chloride of calcium, because experience with it has been more satisfactory. The disinfectant properties of sulfite liquor are also exposed to grave doubt.

"The utilization of sulfite liquors for tanning extracts was not mentioned by the *Frankfurter Zeitung*, therefore there was no reason to refer to them. The writer referred to said he was familiar with the extent to which among tanners and leather chemists, controversy rages for and against their use. It is therefore the work of these trade authorities to collect the results of experience in this new field. If the new tanning extract proves satisfactory, the German technique can be trusted to make use of it because for the tanning substances now most in use duty must be paid. On sulfite liquor-tanning extract from abroad duty would also have to be paid."

"SACCHULOSE"

It is well known that the industrial utilization of the alternative chemical substances which wood is capable of yielding has received a new impetus by the application of several processes. A. Zimmermann (*Chem. Trade J.*, 51, 588) discusses the "Classen process," as used in England. In this process sawdust is subjected in closed retorts to digestion with a weak solution of sulfurous acid and under a pressure of about 6 to 7 atmospheres. Of the resulting product, sugar is an important constituent, of which it contains about 25 per cent. This sugar is drawn equally from the soluble and insoluble carbohydrates; it is dextro in part and is fermentable to the extent of about 80 per cent., the rest being pentose. So far it has not been possible to obtain a crystalline sugar on a commercial scale. According to the original scheme, the sugar produced was, in effect, worked into alcohol, and the maximum yield was about 30 to 35 proof gallons per ton of wood. The English Spirit Act of 1880 contains, however, so many restrictions in the manufacture of spirit from anything but the conventional sources that it was found to be practically useless to pursue the matter. Zimmermann has found wood sugar, or "sacchulose," to be of value as an article of food, particularly as a feeding-stuff for horses, and states that a probable use is also in the preparation of caramel. According to his findings, a factory capable of treating 200 tons of sawdust per week can turn out between 300,000 and 400,000 gallons of proof spirit per year. This also gives by-products of 50 tons of acetic acid, 10 tons of furfural, and 2,000 gallons of methyl alcohol for recovery.

NOTES AND CORRESPONDENCE

A STANDARD VISCOSIMETER AND STANDARD METHODS FOR DETERMINING VISCOSITIES—WHY NOT?

Editor of the Journal of Industrial and Engineering Chemistry:

Although the unsatisfactory condition which exists in this country, in the determination of the viscosities of lubricating oils, was emphasized in the report of Committee D-2 on Standard Tests for Lubricants (*Proc. Am. Soc. Testing Materials*, 10, 117-146), no action has since been taken to improve the situation. The writer does not know just what official action could best be taken, but he believes that he expresses the opinion of most chemists interested in the oil-distributing industry, when he states that the condition is eminently unsatisfactory.

Aside from the use of a large number of types of viscosimeters, which must of necessity occasion unnecessary work in checking up oils for specifications, there is the more serious defect, that no adequate provision seems to be made for standardizing viscosimeters of a given kind. The data included in the report (*Ibid.*) show that variations of 20-30 per cent. in the viscosities reported by the different analysts, for the same oils under the same conditions, are not infrequent. It would seem that differences as large as these must be due, in the main, to a lack of agreement between the viscosimeters. In the relatively small number of comparative tests which the writer has had with other analysts, checks within 3 per cent. as a maximum variation have been obtained. Each analyst with his own viscosimeter would, of course, get values agreeing to 1 or 2 per cent.

The situation in Germany, in particular, would seem to be much better. The almost universal use of Engler's viscosimeter, together with the provisions made for its accurate construction and standardization and with the reference tables such as those of Ubbelohde, must insure better working conditions for the trade. From these tables it appears that the extreme variations for different instruments are 4 per cent. (50-52 seconds water value at 20°). Moreover, by employing the certified water value, which may be checked from time to time, it is possible to obtain from the tables, the Engler numbers, or the corresponding absolute values, which are certainly accurate to a much smaller percentage. The saving of time made possible by running only 50 or 100 cc. of oil, and also the possibility of checking the regularity of the course of a determination, are desirable features, which the use of the tables affords.

Since the Saybolt instruments are not obtainable in the open market, and the Tagliabue instrument seems to be unreliable and faulty in design (Report of Committee D-2, *Ibid.*), it would seem desirable that the Engler viscosimeter be adopted in this country. One or two objections may be advanced against the Engler, but these are unquestionably more than offset by its many advantages. The recommendation of Ostwald's viscosimeter by Dunstan (*J. Soc. Chem. Ind.*, 31, 1063-4) would probably not be received favorably by the trade here, although his suggestion that determinations be made at several widely differing temperatures, is a good one (now complied with to a certain extent). The results obtained by Ellis (*Mel. Chem. Eng.*, 10, 546) should be especially valuable if a satisfactory apparatus, such as Engler's, were adopted, provided that the Temperature-Viscosity Law proves to hold for oils of widely different character. In this connection, it might be stated that a more definite conception of the "temperature of complete solidification," and a full description of the proper method for determining this value, are desirable.

Curves similar to those obtained by Gray (*Original Communication*, Eighth International Congress of Applied Chemistry, 10, 153-8) are useful, and have been employed in our laboratory for some time, but their usefulness is impaired by the lack

of uniformity between different viscosimeters of the same type.

Until some reliable standard instrument is adopted, it would seem useless to attempt the preparation of tables and curves, analogous to those of Ubbelohde. This conclusion is based upon the unsatisfactory data obtained by Committee D-2, and on the failure of data obtained in our laboratory to check even approximately with some of the curves given in the report (*Ibid.*).

Fig. 12, in the report, is improperly labeled, and some of the curves do not check with the data, owing to the fact that the proof was not submitted to the chairman, Dr. Gill, and the publishers saw fit to change the cuts submitted to them. (Private communication from Dr. Gill.) Fig. 13, showing the relations between the different viscosimeters at 212° F., indicates that the Saybolt Universal values should be somewhat more than twice those obtained with the Saybolt C instrument. The following values, taken from our note-books, are not in accord with this requirement. In these tests, no precautions other than those usually observed for maintaining constant temperatures, measuring the oil, and taking the time with a stop-watch, were taken.

TEMPERATURE 210° F.

OIL	SAYBOLT C	SAYBOLT UNIVERSAL
D. W.	40"	42"
P. A.	42 1/2"	46"
P. R.	54 1/2"	55 1/2"
E. F. G. ¹	134"	127"
C. S. ¹	148"	132"
M. S. R. ¹	233 1/2"	227 1/2"

¹ These values were not obtained from the same sample of oil, but from different lots of the same oils, which have always shown only small variations from lot to lot.

Dr. Gill kindly had a sample of P. R. (from the same lot) run in his laboratory, and reported a viscosity of 54 3/5" at 210°, Saybolt C. He checked our Universal viscosimeter at 100° F., and we have also had several satisfactory checks with technical analysts on both the Saybolt C and Universal instruments. It is improbable, however, that satisfactory checks would be obtained with any large number of analysts, in view of the lack of concordance indicated in the above mentioned report.

The writer has written this note for the purpose of once more calling attention to the unsatisfactory condition in the determination of viscosities, and trusts that others may interest themselves to the extent of working out some adequate solution of the difficulty.

W. F. FARAGHER

LABORATORY OF THE ALDEN SPEARE'S SONS CO.
BOSTON, Jan 15, 1913

THE USE OF A LIGHT FILTER CELL IN POLARIZING HIGH GRADE SUGARS¹

Explicit directions for the polarization of sugars as to normal weight, graduation of sugar flask, clarifiers, temperature of polarization, and the sources of light, are given by the International Commission for Uniform Methods of Sugar Analysis but no mention is made of a light filter cell to be used with the prescribed sources of white light. It may be deemed by some a necessity too well known to be mentioned, yet many sugar chemists do not know that without its use an error is introduced. The purpose of the light filter cell is to correct the difference in rotation dispersion between sucrose and quartz. The blue and violet end of the spectrum causes the greatest amount of rotation dispersion and these rays are easily absorbed when the light is passed through a solution of neutral bichromate of potash.

¹ Read at the 7th meeting of the International Commission for Uniform Methods of Sugar Analysis held in New York City, September 10, 1912.

Dark colored sugar solutions naturally tend to purify the light but with light colored solutions there is little purification. When these blue and violet rays are not cut off the polarization is always higher than when they are removed. In some cases an increase of as much as 0.3° V. has been noted. Schönrock¹ noted an average increase with some observers of 0.127° V. He recommends as a filter a 6 per cent. solution of bichromate in a cell $1\frac{1}{2}$ cm. long. Browne² found that the average difference between the readings of the lowest of 4 observers, when using a 3 per cent. solution in a 3 cm. column, was 0.03° V. while with no cell it was 0.22° V. and with a 1 per cent. solution in a 3 cm. cell it was 0.08° V. From this it is seen that results are made concordant by the use of a 3 per cent. solution in a 3 cm. column or by using a solution of such strength that the percentage multiplied by the length in centimeters is 9.

Most makers of polariscopes include in their apparatus either a light filter cell or a crystal of bichromate placed in the ocular but in their directions accompanying the instruments no particular mention is made of the use of the cell. Letters addressed to foreign sugar chemists regarding the use of a light filter cell brought the following replies.

Dr. A. Herzfeld, of the Institute for Sugar Industry, Berlin, Germany, writes:

"The bichromate filters in small tubes were introduced by me more than twenty years ago and that first in the Peters' instrument and later they were taken up by Schmidt and Haensch. They are not absolutely necessary in the investigation of colored sugar products by means of the half shadow instrument but they are absolutely necessary in the case of colorless sugar solutions. We use a $1\frac{1}{2}$ cm. layer of a 6 per cent. bichromate solution. * * * We remove the bichromate solution from the apparatus only in case very dark solutions are being examined in which it is just possible to adjust to a half shadow. I believe that the use of the ray filter cannot be avoided in electric or acetylene lights with colorless sugar solutions. A solution is always to be preferred over solid crystals, since it can easily be removed or renewed."

Dr. F. Strohmer, of the Chemical-Technical Experiment Station for the Austrian Beet Sugar Industry, Vienna, Austria, writes:

"We always use a bichromate cell in our polarization apparatus which is placed between the polarization apparatus and the source of light. * * * We have always had the best success with this arrangement and no differences at all have ever occurred. As a source of light we use a strong Auer or Nernst light and with such mixed lights I consider this arrangement necessary since by means of it the light, which is finally polarized, is homogenized."

Mr. H. C. Prinsen-Geerligs, of Amsterdam, Holland, writes:

"The two hundred odd sugar laboratories in Java are organized and have the following rule:

"When moving the screw for the exact quality of color, the difficulty is often encountered that at the equal shading of the two halves of the discs, the color of both is not exactly the same, one-half possessing a red and the other a blue tinge. This very troublesome phenomenon, which hinders the exact ascertaining of the proper equality, is especially met with in the case of colorless or feebly colored solutions having to be polarized and is due to small differences in the optical properties of sucrose and quartz. In the old apparatus this trouble was neutralized by inserting a plate of transparent potassium bichromate in the ocular which absorbs the blue and violet rays and imparts a yellow color to the disc. In modern apparatus the plate is replaced by a solution of bichromate which is poured in a short observation tube of a very wide diameter which is inserted in the polarimeter between the lamp and the lens and which may

be taken out to be made afresh. Working with sources of white light, i. e., unfiltered electrical, Argand, Auer, kerosene and acetylene light, every separate observer finds values which are identical for his eye but which alter experiments made by Schönrock may differ by 0.008 to 0.127° V. with those obtained by other operators when the polarizations are about 100, which clearly shows that by no means polarizations should be made with unfiltered white light. These differences disappear well nigh entirely if the light from the above mentioned sources is purified by allowing it to pass through a 6 per cent. solution of potassium bichromate in a layer of 6 cm. Hereby the difference in color between the two halves of the disc after the fixing of the just position, which is caused by the difference in dispersion between sucrose and quartz, is almost totally neutralized. In order to obtain by different operators fully concurring figures, it is indispensable to apply the aforementioned tube with potassium bichromate solution. Only in case the polariscope is not equipped with such a contrivance a plate of bichromate is to be inserted in the ocular. When polarizing dark colored solutions, the bichromate solution may be more diluted but it should never be left out."

"You see we are rather strict in Java."

Dr. H. Pellet, of Paris, France, writes:

"For the saccharimeter of the Schmidt and Haensch kind, it is necessary to use a light, slightly colored yellow by means of a cell of bichromate of potash more or less concentrated."

Dr. C. Fischma, member of the Board of Directors of the All-Russian Sugar Association, Kiebr, Russia, writes:

"We in Russia have no legal regulations concerning the use of bichromate of potash in sugar determination by polarizing. In the Association laboratory, however, a 5 per cent. solution of bichromate of potash is always used for the polarization of white sugar because it makes possible much more accurate polarization. In the polarization of yellow sugars, massecuites and molasses this laboratory does not use this solution."

Dr. Hugh Main, of London, England, writes:

"It is easier to read colorless solutions with a bichromate solution in the polariscope than without it and, therefore, I use it in testing the polariscope with pure sugar and retain it in position for all other polarizations."

In defining the 100 point of the Ventzke scale, the Imperial Reichsanstalt of Germany and the United States Bureau of Standards have adopted the use of this light filter cell. I recommend, therefore, to this Commission the following resolution:

That where white light is used in polarizations, the same shall be filtered through a neutral bichromate of potash solution of such a strength that the per cent. composition multiplied by the length of column in centimeters be 9.¹

A. HUGH BRYAN

SUGAR LABORATORY, BUREAU OF CHEMISTRY
U. S. DEPT. OF AGRICULTURE

THE ANALYSIS OF UNSWEETENED EVAPORATED MILK.

Editor Journal of the Industrial and Engineering Chemistry:

We have had considerable difficulty in the fat determination of unsweetened evaporated milk by the Babcock method. To obtain good results directly on the milk, without modification in the manipulation, is an impossibility. Working on the diluted sample does not give satisfactory results. The Gottlieb method gives fair results, but it has been shown² that these results are uniformly low.

The method advocated by the Indiana Experiment Station in *Bulletin 134* gives good results, but they are not always uniform, much depending upon the milk with which one is dealing. The amount of acid, 17.6 cc., given in the method is too much in many cases.

¹ The Commission unanimously adopted this resolution September 10, 1912, at its Meeting in New York City.

² Indiana Expt. Sta., *Bull.* 134.

¹ *Zig. Ver. d. Zuckerind.*, 54, 521-58 (1904).

² U. S. Dept. Agr., *Bur. Chem.*, *Bull.* 122, p. 222.

The following method, we have found, gives uniformly good results on all kinds of unsweetened evaporated milk.

I. MIXING THE SAMPLE

The sample is mixed by shaking, pouring and stirring; some globules of fat persist in staying unmixed; by looking across the surface of the milk with the eye in such a position that the light is reflected to it from the milk, one can easily detect these small chunks of fat and see whether the sample is homogeneous. If these chunks of fat will not mix, warming slightly (not over 40° C.) will help, or sometimes a sample will be met with that needs a very small pinch of caustic soda to aid in emulsifying the fat.

II. FAT

Weigh 4.5 grams of the well mixed sample into a 10 per cent. Babcock milk bottle. Add commercial sulfuric acid (sp. gr. about 1.8) of the same temperature, mixing the two with a whirling motion until a dark chocolate color is produced. From six to eight cubic centimeters of acid are usually necessary. Place the bottles in boiling water and heat for from fifteen to twenty minutes. Remove and let stand until nearly cold. Fill the bottle two-thirds full of hot dilute sulfuric acid (1 volume of water to 1 volume of the concentrated acid), and mix well. Place in the centrifuge and whirl five minutes. Fill to neck with hot half-strength sulfuric acid and whirl three minutes. Add hot water to bring the fat column into the neck of the bottle and whirl two minutes. Read at 120° F. to 125° F. from the bottom of the column to the extreme top of the meniscus. The reading multiplied by four gives the percentage of fat.

NOTES ON THE METHOD

1. In the condensing process the casein becomes toughened so that it is extremely difficult to get it dissolved in the sulfuric acid. The heating in the bottle with the sulfuric acid, and subsequent standing, aids in this process.* There is little danger of charring if the correct amount of sulfuric acid is added.
2. If hot water is added before whirling, in most cases a precipitate forms which interferes with the determination. The addition of half-strength sulfuric acid prevents this.
3. Four and one-half grams were found to be the best amount with which to work.
4. The results obtained by this method have been very gratifying, giving uniformly good, clear readings that check well.

III. TOTAL SOLIDS

Weigh 1 gram of the well mixed milk into a tared aluminum milk dish. Add 25 cc. of water and evaporate to dryness on the steam or water bath. Dry to constant weight in a steam or water oven.

This method was found more satisfactory than making up a diluted sample of known strength and obtaining the sample for solids from it. It is simple and easy to manipulate.

KANSAS STATE AGRICULTURAL COLLEGE
MANHATTAN, Sept. 18, 1912

C. A. A. UTT¹

THE DETERMINATION OF "VOLATILE" IN COAL

Editor of the Journal of Industrial and Engineering Chemistry:
Much interesting and ingenious work has been done during the last two or three years on the determination of "volatile" in coal. It seems to me that his work is mistaken in that it attempts to patch up an inherently faulty method. The following determinations illustrate the weak point in the method.

These determinations were all made by the "official" method except that the flame was protected, and a Tyrell burner and a pipe clay triangle with projections were used.

In every case the flame was over 20 cm. in height and a good non-smoking flame. In No. 2 a Fletcher burner was burning on the same gas pipe as the determination but was put out before No. 3 was started; the regulators of gas and air on the burner were in the same position in each case.

Here are a number of analyses made with ordinary care, all complying, except as noted, with official directions and yet

¹ Assistant Chemist Kansas State Board of Health.

there is a variation of 1.58 per cent. between the highest and the lowest. A rule should be so expressed that if it is followed good results *must* follow. It is not enough that good results *may* follow. It is, to say the least, conceivable that there would be greater difference of conditions in any two given laboratories than prevailed in my laboratory at the time when the Fletcher burner was burning and when it was not.

		Percentage volatile
No. 1	Very little gas.....	{ 20.90
		{ 21.20
No. 2	More gas than No. 1.....	{ 20.95
		{ 21.41
No. 3	Slight increase of gas over No. 2.....	{ 21.70
		{ 22.17
No. 4	More gas than No. 3.....	{ 21.40
		{ 21.65
No. 5	Same gas as No. 4—more air.....	{ 22.08
		{ 22.18
No. 6	Burner pushed to its utmost.....	{ 22.30
		{ 22.48

In my regular work I have always used a three-tube compound burner and have never had any difficulty in getting results agreeing within 0.2 per cent., the average difference between duplicates being 0.1 per cent. By my method the foregoing coal showed 22.67 per cent. and 22.57 per cent. I had attributed the close agreement of my results to the fact that all the coals which came under my observation were high-grade steam coals, New River or Pocahontas. I now believe that my method is, in part at least, responsible.

It is noticeable that as the results approach the limit, the agreement becomes better and it seems not unreasonable to infer that it is easier to get results when all the volatile matter is driven off than to stop at some point short of that result.

I am aware that the phrase "all the volatile matter" sounds loose and unscientific, but the following determinations show that there is a point not easily overstepped to which that definition may be applied.

The same coal was heated for increasing lengths of time according to my method, with the following results:

	Percentage volatile
8 minutes.....	{ 22.64
	{ 22.55
9 minutes.....	{ 22.53
10 minutes.....	{ 22.85

Applied to an anthracite coal, my method gave the following results:

	Percentage volatile
7 minutes.....	{ 5.00
	{ 4.98
8 minutes.....	{ 5.02
9 minutes.....	{ 5.00

Applied to a gas coal, the results were:

	Percentage volatile
7 minutes.....	{ 37.31
	{ 37.48
8 minutes.....	{ 37.58

The slightly higher results which my method gives were not due to entrainment of solid particles. Both determinations gave:

	Percentage ash
Official method.....	4.40
In sample heated ten minutes.....	5.45

One thing that has been impressed on me during these experiments is the difficulty of judging, and consequently, defining, the heating power of a flame. I determined the first coal, a New River coal, and the anthracite with an ordinary Bunsen burner which I expected would give very low results. I obtained:

	Percentage volatile
New River coal.....	21.60
	21.65
Anthracite.....	4.75
	4.60
	4.85

I tried determinations on these coals with the addition of

kerosene, as suggested by Professor Parr,¹ and obtained 22.67 per cent. and 4.93 per cent., respectively. The addition of 7.6 per cent. water did not affect the accuracy of my results, but the addition of 22.8 per cent. water raised the percentage of volatile in the anthracite to 5.21 per cent. and 5.30 per cent., and in the New River coal to 23.00 per cent.

In view of the very limited number of coals at my disposal, I can only consider these figures as indications, but these indications certainly are that the rule for volatile determinations should be so altered as to compel the employment of sufficient heat. That an ordinary Bunsen burner does not give sufficient heat and that such an alteration in the rule would eliminate many sources of error.

I have spoken of heat. I do not know that my better results were not due to the fact that my crucible was well surrounded by reducing gases, but whatever the proximate cause, the ultimate cause was sufficiency of flame.

I am well aware that most chemists will hesitate to discard a process which has been in use so long, but any one who will take the trouble to read the modest disclaimer of the committee which suggested the method² will, I think, agree with me that it would be better to make a drastic revision of the rule in the sense, say, "heat at such a temperature that constant weight is reached in seven minutes," than to continue in the old unsatisfactory rut or bother with petty details.

I assume, of course, that the indications of this work are borne out in a more extended field.

I believe that I have shown that the rule for determination of volatile is not sufficiently explicit. The indications are that a more powerful burner than an ordinary Tyrell burner will give results a little higher, more concordant, and probably more significant. That the use of the larger burner makes the presence of ordinary amounts of water a matter of indifference.

That the use of the larger burner obviates the necessity for the use of kerosene. That a determination with the larger burner requires less care in regard to the time of the determination.

Since I wrote the foregoing, Messrs. Fieldner & Hall have published an article on the "Influence of Temperature on the Determination of Volatile Matter in Coal" in the Proceedings of the Eighth International Congress of Applied Chemistry. I have not yet had a chance to see this article.

FRED C. WELD

65 MERRIMAC ST., LOWELL, MASS.
October 15, 1912

NEW CHIEF OF BUREAU OF CHEMISTRY

Carl L. Alsberg has been appointed Chief of the Bureau of Chemistry, United States Department of Agriculture, to succeed Dr. Harvey W. Wiley, resigned.

Dr. Alsberg was born in New York City, in 1877, and is the son of Meinhard Alsberg, a prominent chemist and one of the founders of the New York Chemical Society from which the American Chemical Society developed.

Carl L. Alsberg entered Columbia University in 1892 and received the degrees of A.B. (1896) and A.M. (1900); he also received the degree in medicine from the College of Physicians and Surgeons. During his residence in the medical school he became interested in biochemical research, and subsequently went abroad to study Pharmacology with Schmiedeberg,

Physiological Chemistry with Hofmeister and Hospital work with Naunyn, all at Strassburg (1900-1902) and later spent a year at the University of Berlin under Emil Fischer and in plant physiology under Kny. One vacation was spent at Frankfurt a/M with Ehrlich, Edinger and Noorden, and another in clinical medicine with Kuttner, Piorkowski and others.

Since returning from Germany, Dr. Alsberg has served as Assistant in Physiological Chemistry in the Medical School of Harvard University (1902-1905); Secretary of the Section of Physiological Chemistry of the International Congress of Arts and Sciences, St. Louis Exposition; Instructor and Head of Department of Biological Chemistry, Harvard Medical School (1905-1906); Faculty Instructor and Head of Department of Biological Chemistry, Harvard Medical School (1906-1908); Chemical Investigator of United States Bureau of Fisheries, investigating food values of sea foods (summers 1906-1908); Chemical Biologist in charge of Poisonous Plant Laboratory, Bureau of Plant Industry, U. S. Department of Agriculture (1908); Past Sec-

retary and member of Council Boston Society of Medical Sciences; Chairman Section of Biological Chemistry of the American Chemical Society; Fellow of the American Association for the Advancement of Science. He is also a member of a number of scientific societies including The American Chemical Society, The American Physiological Society, the Society of Biological Chemists, the Society of Experimental Biology and Medicine, the Society of Pharmacology and Experimental Therapeutics, the American Pharmaceutical Association, the Washington Academy of Science; an associate member of the American Medical Association and the American Association of Cancer Research; and a member of the Corporation of the Marine Biological Laboratory at Wood's Hole, Massachusetts.



DR. CARL L. ALSBERG, NEW CHIEF OF BUREAU OF CHEMISTRY

¹ THIS JOURNAL, 3, 900.

² J. Am. Chem. Soc., 21, 1116, et seq.

ELECTROLYTIC COPPER REFINING IN NORWAY

Consul General Charles Adams Holder, Christiania, states that for several months a company at Aamdal, Norway, has been successfully extracting copper from the crude ore by an electrolytic process invented by Victor Hybinethe, a Norwegian engineer, who has patented the process in Europe and the United States. The Aamdal works have proved so successful that plans are now under way for increasing the output to 3 tons of metallic copper per day.

The treatment, which is done at the mine and thus results in enormous shipping economies, consists in leaching the crushed ore with a solution of sulfuric acid which dissolves out the copper; a strong current of electricity is then passed through this solution and the pure copper is precipitated.

Experiments with copper pyrites from the Orkla and Sulitelma mines, in which much foreign capital is invested, have been equally successful, and as a result will probably be treated by the Hybinethe process in the future. The ores were formerly shipped to Germany and Sweden, respectively, owing to their refractory character and to the lack of proper Norwegian reduction works, but of late the Sulitelma company has not been able to mine with any profit by this plan, owing to the low price of copper and the costs of transportation. The new process will, therefore, mean a great deal to the copper industry of Norway.

GROWING USE OF AMMONIUM SULPHATE IN CHINA

Vice-Consul Charles F. Brissel, Amoy, reports that for many years Manchurian bean cake has been extensively employed as a fertilizer in the vicinity of Amoy, but since 1903 the use of sulfate of ammonia has become more common. To use the bean cake the farmer must pound the large cakes to a dust which must be soaked in water for three days before it can be used. The sulfate of ammonia dissolves in water almost immediately and thus can be used with greater facility. Of the two kinds of sulfate of ammonia, the pure white and the gray-eddish mixture having a strong odor, the latter is the kind used. Sulfate of ammonia is used in the Amoy district principally for fertilizing rice and sugar-cane fields. It is said to have four times the strength of the bean cake and to cost but three times as much, which, taken together with the added facility of application, creates a growing market. In 1903 a trial shipment of 53 pounds was received at Amoy. The reports for 1911 were 7,000 long tons, and up to October 31st the imports for 1912 amounted to about 9,000 long tons. The duty is 5 per cent. Sulfate of ammonia is imported in bags weighing about 175 pounds.

Vice-Consul Raymond S. Curtice, Dalny, Manchuria, states that the enormous output of the Fushun collieries is causing the owner, the South Manchuria Railway, no little anxiety, as the actual and probable demands do not justify the expectation that they will equal the output. Accordingly the manufacture of by-products has become a necessity. It is now proposed to begin the manufacture of sulfate of ammonia and producer gas. It is claimed that 100 tons of Fushun coal can produce 5 tons of sulfate of ammonia in addition to a large amount of gas. It is intended to put the sulfate of ammonia on the Japanese market in competition with the foreign variety, which totals about \$5,000,000 a year. The competition will, of course, practically drive the foreign products out of the market, as the Fushun collieries will have an unlimited supply of both material and fuel. The gas will be used for the generation of electric power.

AMERICAN CHEMICAL SOCIETY SPRING MEETING.

The Spring meeting of the American Chemical Society will be

held in Milwaukee, March 25th to 27th, inclusive. The Council will meet on the evening of March 25th. The titles of all papers intended for the meeting should be in the hands of Secretary Charles L. Parsons, Box 505, Washington, D. C., by March 7th, or in the hands of the secretaries of the various divisions by March 5th; otherwise they cannot find place on the program.

"THE PROGRESSIVE AGE" BECOMES "THE GAS AGE"

We note with pleasure the change indicated in the above title. The publishers are to be congratulated on this improvement since it is a step towards standardization of scientific current literature, both in size and name. The general appearance, composition, paper and printing of *The Gas Age* are noticeably in advance of its predecessor.

OBITUARY—ALFRED BELLAMY AUBERT

Professor Alfred Bellamy Aubert, one of the oldest members of the American Chemical Society, for thirty-five years professor of Organic Chemistry and head of the Department of Chemistry, University of Maine, died at his home, 118 East 62nd Street, New York City, November 12, 1912. He was born in New York of Alsatian parentage, in 1853. He received his chief undergraduate training at the Imperial Lyceum of Strasbourg; specialized in Chemistry, under Crafts, at Cornell University, receiving the B.S. degree (1873) therefrom, and the M.S. degree (1874) from the University of Maine; engaged in chemical research, 1899-1900, Massachusetts Institute of Technology. Dr. Aubert was a frequent contributor to the *Journal of the American Chemical Society*; *Chemical News*; *American Monthly Microscopical Journal*; *Photographic Times*; *Chemical Engineer*; *Le Diatomiste*; *La revue generale de Chemie*; and co-editor with Dr. Allen Rogers of a work on Industrial Chemistry. Under special ruling he became a recipient of a Carnegie pension for teachers.

Intellectually and professionally, Dr. Aubert was strongly equipped, of keen insight, an artistic, accurate, rapid and resourceful laboratory worker and investigator. Broadly cultured, philosophic, a linguist, master of a clear, crisp yet polished English, he was nevertheless unambitious and careless of his great gifts. For this reason, and from ill health, only his associates knew his real worth; also for these reasons his contributions to English and French journals in his special fields of Chemistry and Microscopy were, though occasional, all too few. Probably of most of his work he made no notes. Of some there were outlines, left unfinished, as was his latest projected book—"The Microscope in Chemical Analysis and Research." His "Industrial Chemistry," of which he was the originator, associate editor and partial author, long projected, delayed, and personally unrevised because of failing strength, was issued but shortly before his death. It was probably the first definitely planned, though not first issued, of the recently appearing treatises in this chemical field, to embody the symposium-of-experts method.

In personality, Professor Aubert was as artless and open as a child, and evidenced a great and sympathetic heart, obvious to all who met him. For his intimate friends he had a passionate attachment which gripped them in unseverable bonds. Over his pupils his gentle sway was complete and time-enduring. For them his wide culture, accurate knowledge and enlivening scientific imagination were rich resources of profit and delight. To have met him was a privilege; to have known him was a life's enrichment; to have sat at his feet was an abiding inspiration. "We shall not look upon his like again."

W. F. JACKMAN

BOOK REVIEWS

A Handbook of Sugar Analysis. A practical and descriptive treatise for use in Research, Technical and Control Laboratories. By C. A. BROWNE, Ph.D., chemist in charge of the New York Sugar Trade Laboratory (formerly Chief of the Sugar Laboratory, U. S. Bureau of Chemistry, Washington, D. C., and Research Chemist of the Louisiana Sugar Experiment Station, New Orleans, La.). John Wiley & Sons, New York and London. 8vo. 977 pages, 200 figures. Cloth, \$6.00 net.

This unusually thorough and able treatise upon sugar analysis has been prepared by the author in recognition of the great expansion of knowledge of the subject within the past quarter century with the devising of instruments of greater accuracy, the improving of old methods and the discovery of new ones.

The range of sugar analysis is so broad that in the selection of methods the author has been guided by his own experience—a very extended one—in various research, technical and control laboratories.

In order to correct the tendency of inexperienced workers to make general use of methods having only limited applicability, the author has included with the description of each method a brief account of its applicability and limitations.

A rather novel feature is the account in Part II of the sugars themselves, their occurrence, properties and methods of synthesis, which is often of use in determining their individuality. The practical nature of the book is indicated in the first chapter, which immediately takes up the sampling of sugar and sugar products, discussing the best methods as well as the influences which affect the samples.

The various methods of determining moisture are next taken up and very fully discussed, with thorough accounts of the apparatus employed and the derivation of formulas for specific gravity, temperature, etc.

An interesting chapter on the refractometer and its use in sugar analysis follows, which presents this recently developed method with thoroughness.

The next two hundred or more pages deal with polarized light, polarimeters, saccharimeters, polariscope accessories, specific rotation of sugars, methods of simple and of invert or double polarization as well as special methods of saccharimetry. The wealth of material gathered here is great and its ready applicability very satisfactory. In the miscellaneous physical methods as applied to the examination of sugars are interesting discussions of viscosity, specific heat of combustion, osmotic pressure constants and displacement of freezing and boiling points. All these are treated mathematically as are all the other topics requiring such elucidation, and this will be found one of the most appreciated features of the work, placing the discussions on the highest plane of scientific treatment. The author says that probably no other class of organic compounds gives such a variety of reactions or forms so large a number of chemical derivatives as the sugars, and he proceeds to describe the many reactions of use in identifying the sugars, generically and individually. Eighty pages are next devoted to the reduction methods for determining sugars, with great detail as to reagents and manipulation, variations due to many causes and collateral matter of importance in the analytical methods described. Another chapter describes methods for the quantitative determination of pentoses, etc., the fermentation methods of determining sugars, the various colorimetric methods and methods of determining sugars by weighing as hydrazones and osazones. Combined methods and the analysis of sugar mixtures are treated with formulae, tables, examples and explana-

tions. This is one of the most exacting fields in sugar analysis and will be found very well set forth.

Under miscellaneous applications are considered the routine analyses of sugar factory products not previously dealt with, as ash, quotient of purity, extraction of juice from cane and beet, acidity and alkalinity, as well as methods for determining crystal contents giving preference to that of Koydl. Starch, dextrine and malt extracts analyses are briefly considered as well as maple sugar and syrup, fruits products and honey. The author usually indicates the most reliable of the methods given, with reasons for its preference.

The second part of the work, two hundred and sixty pages in extent, is devoted to a discussion of the occurrence, methods of preparation, properties and principal reactions of the thirty or more sugars which have been isolated from plant and animal substances and of their many allied derivatives. Beginning with the classification of the sugars and their formation in nature, the author explains the optical activities of the asymmetric carbon compounds. The various monosaccharides are next described with especial attention to Arabin, xylose, fucose and rhodose before taking up very fully, as their importance deserves, the hexoses including the glucoses, mannoses, starch, pectins, galactoses, etc.

Under the disaccharides, of course, sucrose occupies the place of prime importance and its physical, chemical and biological properties are carefully discussed in considerable detail. The action of enzymes on sucrose constitutes not the least interesting feature of this chapter. Maltose, representing like sucrose, important manufacturing interests, receives detailed consideration and lactose is not far behind in this respect.

The trisaccharides and tetrasaccharides are principally represented by raffinose, and stachyose, the former of which comes in for extended attention.

The amino sugars, of considerable theoretical interest, because of their forming one of the connecting links between the carbohydrates and the proteids, are described, as well as the cycloses, which are widely distributed in nature and form a connecting link between the sugars and the aromatic benzole ring derivatives. Inosites and quebrachite are interesting members of this group.

In the closing chapter of this encyclopedic book the author briefly describes the alcohols and the monobasic and dibasic acids which are derived from the sugars by reduction and by oxidation and which are constantly found associated with them in nature.

Following the text are twenty-five tables, occupying a hundred pages, such as are most generally useful in sugar laboratories. These tables are also published separately for the convenience of those who wish to make frequent use of them in practical work.

One of the interesting features of this book is the considerable amount of the author's original work evinced throughout the volume. His study of moisture absorption and loss by different grades of commercial sugars, his method of vacuum drying and the details of his carefully elaborated arrangements for constant temperature work are all of very practical value. His methods for determining dextrin and commercial glucose in honey and his formulae for analyzing sugar mixtures are admirable evidences of the author's able handling of these intricate questions.

Indeed the entire work is greatly to be commended for its depth and thoroughness, and although it occupies nearly a thousand pages it is concise and to the point throughout. The book is a mine of useful information to all those in any way

interested in the sugars or any of the allied substances. It is a classic of its kind that will always occupy a preëminent place in sugar literature. The hundreds of excellent illustrations add greatly to the text and are quite in keeping with the high character of the volume in all other respects. W. D. HORNE

Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines. By R. M. STRONG AND LAUSON STONE. Bulletin 43, Department of the Interior, Bureau of Mines. 236 pp. July, 1912.

Under the terms of the act establishing the Bureau of Mines, the Bureau interprets its vocation to include the investigation of the liquid fuel resources of the country both with respect to geological conditions and to economic use, and accordingly a series of tests were conducted in great detail on the use of gasoline in small engines, 10 to 15 H. P., and the results are compared with their performance on alcohol as a possible competitor of gasoline. It is the results of these tests that are reported in this bulletin, which contains detailed information and conclusions drawn therefrom, so presented as to constitute a valuable addition to the literature on the subject. The cost of these investigations, undoubtedly very high, would be an interesting consideration especially as there is serious doubt as to whether any commensurate benefit will follow, for without questioning the scientific value of the data, it is believed that it will have practically no influence on either the construction or use of these engines or on the economical relations of gasoline to alcohol as sources of fuel supply. Some of the more important conclusions are abstracted below but these give but an inadequate idea of the report, which should find a place in the library of every engineer and chemist.

The low heating value of completely denatured alcohol averages 10,500 B. T. U. per lb. or 71,900 B. T. U. per gallon, while the corresponding values for gasoline of specific gravity 0.71 to 0.73 are 19,200 B. T. U. per lb. and 115,800 B. T. U. per gallon. Comparing them, the low heating value of one lb. of alcohol is approximately 0.6 of that for gasoline. One lb. of gasoline requires approximately twice as much air for complete combustion as is required by alcohol, so the heating value of 1 cu. ft. of explosive mixture of alcohol-vapor and air, in combining proportions, is approximately equal for gasoline air as for alcohol air at about 80 B. T. U. per cu. ft., standard. The compression that such mixtures will stand without self-ignition in the cylinders of the small four-cycle engines are 70 lbs. per sq. in. above atmosphere of gasoline, and 180 lbs. for alcohol, and in all cases the maximum fuel economy corresponds to the use of these maximum available compressions.

The gasoline engine operating on the maximum available compression of 70 lbs. per sq. in. will when operated at the same compressions of alcohol give an increase of 10 per cent. of the power over that obtained from gasoline, but when the compression is changed to the 180 lbs. per sq. in. which the alcohol will stand, the engine will, on that fuel, give 30 per cent. more horsepower than when operated on 70 lbs. per sq. in., the limiting value for gasoline and on gasoline. With alcohol fuel and the maximum compression pressure of 180 lbs. per sq. in. maximum explosion pressures reach between 600 and 700 lbs. per sq. in., which is greater than small gasoline engines are ordinarily built to withstand, indicating that for the most economical use of alcohol higher compressions are needed and heavier construction will be required than is provided in existing gasoline engines.

The consumption of fuel per hour per H. P. for these small engines operating at the compressions ordinarily used for gasoline are in the ratio of 3 to 2 for alcohol as compared with gasoline, but when each fuel is used at its maximum allowable compression, the volumetric consumption of fuel per hour per H. P. is about the same for alcohol and gasoline and averages about

one pint at the rated load which is ordinarily 75 per cent. to 80 per cent. of the maximum. To secure the best consumption of either fuel at any load requires a hand adjustment of mixture, and time of ignition for each change, and without hand adjustment, engines operated by throttle governors can double their fuel consumption on $\frac{1}{2}$ load. The best fuel consumption found on engines of 10 to 15 H. P. are for gasoline 26 per cent and 28 per cent. on compressions of 70 and 90 lbs. per sq. in. respectively. For alcohol, efficiencies are 28 per cent., 39 per cent., 40 per cent. for compressions of 70, 180 and 200 lbs. per sq. in., indicating a slightly superior efficiency for alcohol over gasoline at the same compression, 28 as compared with 26 per cent. at 70 lbs.

The addition of water to explosive mixtures of gasoline vapor and air does not change the specific consumption for gasoline per hour per H. P. but does decrease the H. P. up to an amount of water equal to that of gasoline by weight. The allowable compression pressure is at the same time raised to about 140 lbs. from 70 lbs. without preignition. Introduction of water with denatured alcohol in quantities up to 50 per cent. increases specific fuel consumption a small amount and decreases the horsepower.

The report contains detailed information on the chemical and physical properties of gasoline and denatured alcohol as fuel and the apparatus and methods used in the test with the details of procedure and the conduct of test and conclusions of a technical character on the variables that control economy, efficiency, time of ignition and character of spark, jacket water temperature, engine speed, load variation, water addition to fuel and decrease of compression on the performance of the machine.

It is proposed in the future to carry out similar tests on the use of heavy fuel oils in internal combustion engines and on the performance of the oil gas producer. The probable cost of proposed tests might be presented to representatives of the industries concerned, for discussion as to the justification for the expenditure compared with the beneficial effects that may be expected to follow.

C. E. LUCKE

Textbook of Chemical Technology and Metallurgy, prepared by the cooperation of distinguished specialists, edited by Dr. Bernhard Neumann, published by S. Hirzel, Leipzig. (German.) 8vo. Price, \$5.00.

Since the title clearly indicated the character of this work, a textbook of Chemical Technology, we should not expect more than a general survey of the field of industrial chemistry and metallurgy. The authors cannot give more than the salient points in connection with each industry, including a few statistics to give an idea of the magnitude and of the growth of that particular line of chemical manufacture.

Accepting this work of Neumann and his collaborators in the above light, we have a book that comes up to the specifications in every respect, and in many chapters the development of the subject gives us more than we have a right to expect in a work of this character and scope.

Some idea of the space devoted to each of the various industries can be obtained from the following, selected at random as showing some of the smaller as well as some of the larger lines of chemical manufacturing: Sulphuric acid 25 pages, coke 10, acetylene 11, soda 29, chlorine 25, iron and steel 39, petroleum 11, rubber 18, glue 4, sugar 32.

The topics discussed, include: Water supply and disposal of waste effluents from factories, liquid air, oxygen, ozone and acetylene, fuels and illuminants, 114 pages; Salt, potash, soda, mineral acids, chlorine by Weldon and electrolytic methods, ammonia and cyanide compounds, 158 pages; Aluminium and compounds, magnesium, calcium, and barium compounds, peroxides and per salts, fertilizer chemicals, mortar, stoneware and porcelain, glass, 131 pages; Iron, steel and nonferrous metals,

139 pages; Explosives, petroleum, asphalt, coal tar and wood products, 67 pages; Fats, glycerine, and soaps, 34 pages; Rubber, glue, and leather, 34 pages; Sugar, starch, dextrine and the fermentation industries, 105 pages; Cellulose and artificial silk 14 pages, and finally, the textile fibers and dyestuffs, 48 pages.

A criticism that is too often applicable to books of this class, that the practice is out of date, cannot be made of the volume before us. One looks carefully for any omissions in connection with the latest developments of chemical industry and finds that the authors have informed themselves of the latest methods in all countries. A possible exception to the foregoing statement might be made with reference to petroleum distillation as modified by American conditions.

In this admirable work, one can find very little to criticize, if the intent of the authors is kept in mind, that of writing a textbook of general information on industrial chemistry and metallurgy. It might be said that the space devoted to the Talbot process of steel manufacture (six lines) is too short. In like manner, we should like to have seen more than a page devoted to alloy steels and their applications, the development of which has certainly produced a marvelous group of new materials for the modern industrial world.

The more important chapters conclude with statistics, which are in most cases brought down to the close of 1910, and which also show the production by countries.

The work comprises 890 pages, with 398 cuts and five plates. All of the figures are up-to-date, and in this connection it is certainly a relief to find that the old cuts, so long familiar because they were copied by generation after generation of textbook writers, have been replaced.

J. H. JAMES

Die Synthese des Kautschuks. RUDOLF DITMAR, Inhaber des Kautschuk-Laboratoriums und der Kautschuk-Chemischule in Graz. 124 + vii pages. Dresden and Leipzig: Verlag von Theodor Steinkopff, 1912.

This little book sketches briefly the work that has been done on synthetic rubber up to 1912. The matter is divided as follows: I. The Constitution of Rubber (23 pp). II. Synthesis of Rubber (9 pp). III. Preparation of Materials used in making Synthetic Rubber (22 pp). IV. The most important patents granted and applied for (70 pp). As the author foreshadows in his preface, the activity in this field of industrial research is such that by the time a résumé of this sort appears in print further progress will inevitably have been made. The monograph has been prepared primarily for the sake of those chemists not themselves actively engaged in this field. The work has been well done and will be read with interest.

THEODORE WHITTELEY

Soil Fertility and Fertilizers. By JAMES EDWARD HALLIGAN. 398 pp., 23 illustrations. The Chemical Publishing Co., 1912. Price, \$3.50.

The preface states that "this book has been written to be in reach of the student, manufacturer, and other persons interested in the subject of fertilizers. Technical terms have been omitted as much as possible."

The book is divided into sixteen chapters: the first treats of the chemical elements needed by plants, and the composition of plants including analyses of the principal agricultural crops.

Chapters II and III deal with the fertility of the soil and means of maintaining fertility.

Chapter IV takes up the question of farm manures and includes much valuable information concerning the composition of the various kinds, value, manner of application, etc.

The remaining twelve chapters discuss the fertilizer question in all of its phases including a very complete description of

the different fertilizer materials, where obtained, method of preparation, etc., together with a large amount of information relative to their functions as bearing on the production of crops.

The subject is a large one considered in all of its bearings, but the author has succeeded in bringing together just such facts as will enable one to get a very clear understanding of the usually accepted views concerning soil fertility and the compositions and functions of fertilizers. The volume is replete with tabulations and statistics which include valuable data concerning the analysis of fertilizers, farm crops, formulae, valuation, etc., which makes it valuable as a general reference book. The data is compiled from reliable sources, and excellent judgment has been used in selecting just such information as will appeal to those interested in the subject. The whole work is a useful one as a general treatise on the subject.

F. B. CARPENTER

Das Hydrosulfit. By DR. CARL JELLINEK. 2 parts, 8vo., pp. vi + 188 and viii + 230. Stuttgart, 1911. Ferdinand Enke. Price, Part I, 1.20 M.; Part II, 1.50 M.

These two monographs form portions of what might be termed a treatise on chemistry, a volume of which is issued each year by Prof. W. Herz, of Breslau.

The first part of the present treatise deals with the pure chemistry of hydrosulphurous acid and its various salts and compounds. The physical chemistry of the subject is also elaborated at considerable length, and with a thoroughness distinctly German in its academic treatment. The second part deals with the preparation and technical chemistry of the various hydrosulphite compounds, and the methods for their analysis.

Whereas the purely chemical side of this subject is treated by the author in an excellent manner, the technical part is dismissed somewhat negligently, showing that the author in this part did not have a good grasp of his subject. In fact the technical matter consists principally of a collection of patents, with all the indefinite verbosity of legal style. As the hydrosulphites are principally interesting by reason of their technical applications, it is to be regretted that the author did not better develop this side of the subject. As a study in pure chemistry, however, the book is exceedingly interesting.

A very good bibliography of the subject is also furnished, as well as a complete list of patent titles relating to the manufacture and use of hydrosulphites.

J. M. MATTHEWS

The Analysis of Paint and Varnish Products. By CLIFFORD DYER HOLLEY, M.S., Ph.D. First Edition. Small 8vo. viii + 292 pp. John Wiley & Sons, New York. 1912. Price, \$2.50.

In the earlier work, "The Analysis of Mixed Paints, Color Pigments and Varnishes" by Holley and Ladd published in 1908, is to be found a large part, probably the major part of the subject matter of the present volume. In some cases the matter is quite identical. There is, however, a considerable proportion of new matter and as a whole it furnishes a valuable work of reference to one engaged in the analysis of paints and varnishes. It is to be regretted that so little space is given to China Wood Oil which is at present one of the most interesting materials entering into the composition of paints and varnishes. Probably each manufacturer of paint or of varnish will find about this volume a different point to criticize as not in accord with his own ideas of the proper methods of testing such products, but the work sets forth with a fair degree of completeness the present state of this art as most analysts come in contact with it. The references to original articles are, however, not nearly as frequent or as complete as the reviewer thinks they should be.

PARKER C. McILHINEY

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York

- Ceramic Chemistry.** By H. H. STEPHENSON. 8vo. Price, \$1.50. Davis Bros., London.
- Chemical Industry of the World, Directory of the.** 2nd edition. 1. 8vo. 1200 pp. Price, \$5.00. Union Deutsche Verlagsgesellschaft, Berlin. (German.)
- Coal-tar and Ammonia, The Industry of.** By G. LUNGE AND H. KOEHLER. Vol. 2. 5th edition. 8vo. 1516 pp. Price, \$12.00. F. Vieweg & Sohn, Brunswick. (German.)
- Coke, The Manufacture of, and the By-products from the Distillation of Coal.** By A. SAY. 8vo. Price, \$3.50. Dunod & Pinat, Paris. (French.)
- Cyanide Practice.** By H. W. MACFARREN. 8vo., 291 pp. Price, \$3.00. McGraw-Hill Book Co., New York.
- Electrochemical Industry of France.** (Translation.) By M. R. PITAVALL. 8vo. Price, \$2.25. Wilhelm Knapp, Halle. (German.)
- Electrochemistry, The Principles of.** By A. J. ALLMAND. 8vo. 527 pp. Price, \$4.50. Edward Arnold, London.
- Electroplating.** By WILLIAM R. BARCLAY AND CECIL H. HAINSWORTH. 8vo. 381 pp. Price, \$2.00. Edward Arnold, London.
- Elements, Detection, Determination and Separation of the Chemical I.** By A. RUEDISUELE. 8vo. Price, \$6.00. Max Drechsel, Berne. (German.)
- Essential Oils: Scientific and Industrial Bulletin.** Roure Bertrand, Fils; Oct., 1912. Sm. 8vo. 191 pp. Roure Bertrands, Fils, Grasse.
- Food: American Pure Food and Drug Law.** By JAMES WESTERVELT. 8vo. 1535 pp. Vernon Law Book Co., Kansas City.
- Food Industry, The.** By K. VON BUCHKA. Vol. 2. 8vo. Price, \$15.00. Akademische Verlagsgesellschaft, Leipzig. (German.)
- Fuels, Liquid, their Production, Characteristics and Examination.** By L. SCHMITZ. 8vo. 168 pp. Price, \$1.50. Julius Springer, Berlin. (German.)
- History of Chemistry from the Earliest Times to the Present Day.** By JAMES CAMPBELL BROWN. 8vo. 543 pp. Price, \$2.75. J. & A. Churchill, London.
- Industry, Chemical, Bluecher's Manual for.** 8th edition, 1912-13. L. 8vo. 1450 pp. Price, \$3.75. Franz Siemsenroth, Berlin. (German.)
- Leather Dyeing and Preparing.** (Translation.) By M. C. LAMB. 2nd edition. 8vo. Price, \$5.50. Julius Springer, Berlin. (German.)
- Mine Fires and How to Fight Them.** By JAMES W. PAUL. 8vo. 14 pp. U. S. Bureau of Mines, Miners' Circular 10.
- Paper Pulp, Dyeing of.** By J. ERFURT. 3rd edition. 8vo. Price, \$3.75. Carl Hofmann, Berlin. (German.)
- Petroleum and Kindred Substances; Vol. IV.** By H. VON HOFER. 3rd edition. Lex. 8vo. 351 pp. Price, \$3.75. F. Vieweg & Sohn, Brunswick. (German.)
- Practical Chemistry, Introduction to.** By F. B. AHRENS. 2nd edition. 8vo. Price, \$1.25. Ernst Heinrich Moritz, Stuttgart. (German.)
- Printing, Textile, The Principles and Practice of.** By EDMUND KNECHT AND J. B. FOTHERGILL. 8vo. 604 pp. Price, \$9.00. Chas. Griffin & Co., London.
- Refractories and Furnaces.** By F. T. HAVARD. 8vo. 356 pp. Price, \$4.00. McGraw-Hill Book Co., New York.
- Sizing, The Materials Used in.** By W. F. A. ERMEN. 8vo. 119 pp. Price, \$1.25. Constable & Co., London.
- Smoke Abatement and City Smoke Ordinances.** By SAMUEL B. FLAGG. 8vo. 57 pp. U. S. Bureau of Mines, Bulletin 49.
- Technology, Chemical, and Metallurgy, Textbook of.** By BERNHARD NEUMANN. 8vo. Price, \$5.00. S. Hirzel, Leipzig. (German.)
- Textile Design and Color.** By WILLIAM WATSON. 8vo. Price, \$2.00. Longmans, Green & Co., New York.
- Water Purification and Sewage Disposal.** By J. TILLMANS. 8vo. Price, \$2.00. Wilhelm Knapp, Halle. (German.)
- Colors Used in the Cement Products and Artificial Stone Industries.** ANONYMOUS. *Farben Zeitung*, Vol. 18, 1912, No. 11, pp. 579-582.
- Concrete, Tests of Waterproofing for.** By CLOYD M. CHAPMAN. *Industrial World*, Vol. 46, 1912, No. 51, pp. 1504-1506.
- Cyaniding Slime Ore by Continuous Decantation.** By H. C. PARMLEE. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 1, pp. 25-28.
- Explosives, The Energy of.** By WALTER O. SNELLING. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 28, 1912, No. 8, pp. 653-683 and *Engineering Record*, Vol. 67, 1913, No. 2, pp. 54-55.
- Fat, The Distillates of Wool.** By J. MARCUSSON AND A. VON SKOPNIK. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 50, pp. 2577-2580.
- Gas, Illuminating, in its Hygienic and Industrial Relations.** By AD SAMTLEBEN. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 51, pp. 2640-2649.
- Gas, Illuminating, Some Notes on the Purification of.** By R. H. BURDICK. *American Gas Light Journal*, Vol. 98, 1913, No. 1, pp. 1-7, 10-13.
- Lead Smelting, The Action of Lime in the Flintshire Process of.** By C. O. BANNISTER AND A. V. ATLEY. *Chemical World*, Vol. 2, 1913, No. 1, pp. 9-11.
- Lubricating Oil, Purchase of, by Specification.** By A. D. SMITH. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 28, 1912, No. 8, pp. 684-722.
- Mercury, A Case of Mercurial Poisoning and the Estimation of, in Textile Materials.** By L. L. LLOYD AND W. M. GARDNER. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 23, pp. 1109-1112.
- Mordants for Dyeing and Printing, Making of.** By T. BROCKLEHURST. *Textile Colorist*, Vol. 34, 1912, No. 408, pp. 311-314.
- Oils, Progress in the Domain of Ethereal, and Perfumery.** By A. RECLAIRE. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 50, pp. 2580-2589.
- Paint-Making Machinery.** By J. R. TORRANCE. *Oil and Colour Trades Journal*, Vol. 42, 1912, No. 735, pp. 1672-1677.
- Patent Law in 1911, Essays on.** By H. TH. BUCHERER, et al. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 49, pp. 2566-2576.
- Patent Protection for Pharmaceutical Products.** By JULIUS EPHRAIM. *Zeitschrift fuer angewandte Chemie*, Vol. 25, 1912, No. 51, pp. 2629-2640.
- Peat for Power Purposes, Commercial Utilization of.** By H. V. PEGG. *Journal of the American Peat Society*, Vol. 5, 1912, No. 3, pp. 163-168.
- Photometry of Incandescent Gas Lamps, The.** By C. O. BOND. *American Gas Light Journal*, Vol. 97, 1912, No. 27, pp. 418-423, 426-427.
- Power-Plant Economics.** By HORACE W. FLASHMAN. *School of Mines Quarterly*, Vol. 34, 1912, No. 1, pp. 1-23.
- Rubber, India, Determination of Total Sulfur in.** By C. E. WATERS AND J. B. TUTTLE. *Bulletin of the Bureau of Standards*, Vol. 8, 1912, No. 3, pp. 445-453.
- Rubber, India, The Action of Gaseous Oxygen on.** By STANLEY JOHN PEACHEY. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 23, pp. 1103-1105.
- Rubber, Natural and Synthetic.** By F. MOLLWO PERKIN. *India Rubber Journal*, Vol. 44, 1912, No. 25, pp. 15-17.
- Rubber, The Nitrogenous Constituent of Para Rubber, and its Bearing on the Nature of Synthetic.** By CLAYTON BEADLE AND HENRY P. HEVENS. *Journal of the Society of Chemical Industry*, Vol. 31, 1912, No. 23, pp. 1099-1103.
- Sewage and Sewage Filter Effluents, Disinfection of.** By H. W. CLARK AND STEPHEN DE M. GAGE. *Engineering Record*, Vol. 67, 1913, No. 1, pp. 14-16.
- Sewage Pumping Machinery and Appliances.** By J. RALPH GIBSON. *Industrial World*, Vol. 46, 1912, No. 53, pp. 1568-1570.
- Sewage, The Purification of Tannery Effluents.** By F. P. VEITCH. *Journal of the American Leather Chemists' Association*, Vol. 8, 1913, No. 1, pp. 10-22.
- Solvents, Physical Constants of some Chlorinated Hydrocarbons Important as.** By W. HERZ AND W. RATHMANN. *Chemiker Zeitung*, Vol. 36, 1912, No. 146, pp. 1417-1421.
- Sugar, Study of the Different Methods of Determining Sucrose in Cane Molasses.** By CHARLES FRIBOURY. *International Sugar Journal*, Vol. 14, 1912, No. 168, pp. 702-712.
- Sulfates, Anhydrous.** By G. CALCAGINI. *Gazzetta Chimica Italiana*, Vol. 42, Part 2, 1912, No. 6, pp. 652-686.
- Sulfur in Illuminating Gas, and its Removal with Special Reference to the Use of Lime.** By L. J. WILLIEN. *Gas Age*, Vol. 31, 1913, No. 1, pp. 5-14.

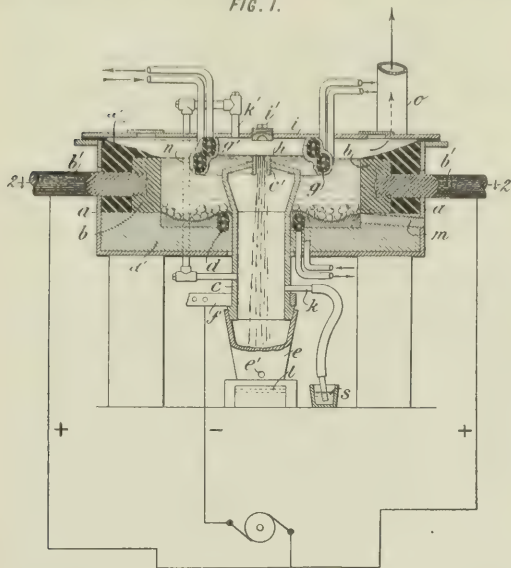
RECENT JOURNAL ARTICLES

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Light Metals, Notably Sodium. Seward, von Kugelgen & von Bidder, Nov. 5, 1912. U. S. Pat. 1,043,154. The purpose of this process is to produce sodium directly by the electrolysis of sodium chlorid. In the apparatus shown, current is led through the casing *a* by means of graphite pencils, *b'*, which are connected with graphite plates, *b*, which fit together to form

FIG. 1.

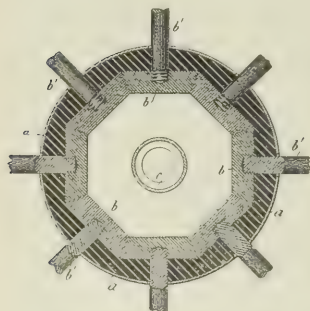


a polygonal anode and also form the sides of the crucible.

By limiting the height of the anode a protective layer of salt may be maintained over the top, preventing oxidation and disintegration of the carbon.

The cathode *c* is made of cast iron. Surrounding the cathode at a point above its entry through the casing is a water-cooled coil, *d*, which serves at once to prevent leakage of electrolyte and limits the activity of the cathode which otherwise would be progressively downward. This coil is embedded in the crucible bottom as shown and also tends to maintain the integrity of the latter by its cooling effect. A nipple, *c'*, in the top of the cathode receives the molten metal as its level rises within the sodium chamber and directs its course so that it will drop clear of the walls of the cathode cavity and fall into the receiver *e*, from whence it may be tapped at intervals through tap-hole *e'*.

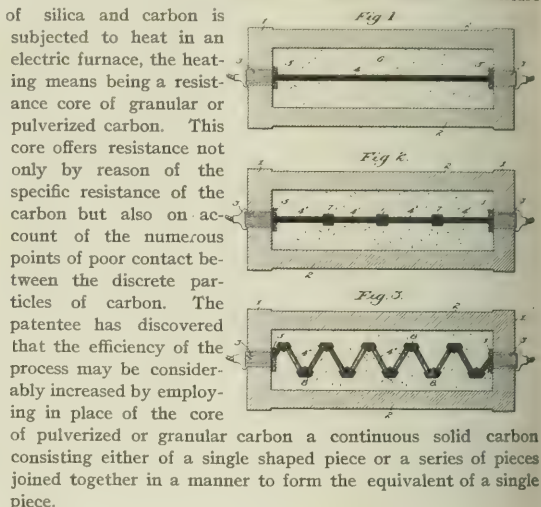
FIG. 2.



The sodium is collected within the water-cooled and salt-incrusted "curtain" *g*, which dips below the electrolyte and divides the space above it into a "sodium-chamber" and a "chlorin chamber." *g* is in no sense a "pole cell" as it is kept totally inactive by the layer of chilled salt, *n*, maintained thereon

through the cooling action of the water circulating within the "curtain." The "curtain" is made of two separate coils of copper tubing which are first covered with a solid insulating material before the layer of chilled salt is applied. Such a preliminary coating will act as an extra insulation in case the layer of salt becomes too thin through irregularities in the run and is conveniently made by closely wrapping two or more layers of strong asbestos twine on the tubes. An opening through the cover *i* at its center gives access to the sodium chamber and to the cathode cavity through the nipple *c'* and is normally closed by the plug *i'*. Other openings through the cover into the chlorin chamber are provided for feeding in salt and for breaking up salt crusts if any form. The chlorin is drawn out through the stack *o*, a slight suction being preferably maintained. The crucible may be quickly emptied when desired through the tap-hole *m*.

Silicon Carbide. F. J. Tone, Nov. 12, 1912. U. S. Pat. 1,044,295. In the commercial manufacture of silicon carbide a mixture of silica and carbon is subjected to heat in an electric furnace, the heating means being a resistance core of granular or pulverized carbon. This core offers resistance not only by reason of the specific resistance of the carbon but also on account of the numerous points of poor contact between the discrete particles of carbon. The patentee has discovered that the efficiency of the process may be considerably increased by employing in place of the core of pulverized or granular carbon a continuous solid carbon consisting either of a single shaped piece or a series of pieces joined together in a manner to form the equivalent of a single piece.



Acetone and Higher Alcohol by Fermentation of Starch, Sugars and Other Carbohydrate Materials. A. Fernbach and E. H. Strange, Nov. 12, 1912. U. S. Pat. 1,044,368. In this process carbohydrate matter is mixed with water and a suitably degraded yeast added. The mixture is then sterilized, a ferment of the type of the butylic bacillus of Fitz added, and the mixture fermented in the absence of air.

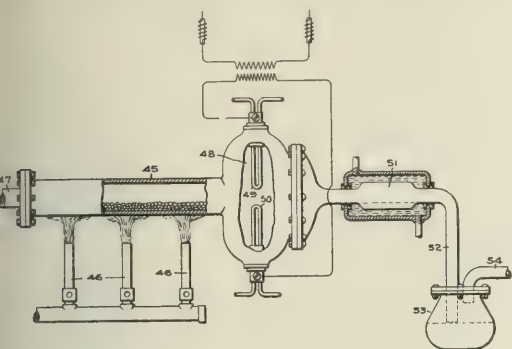
Reducing Chemical Compounds. Ezechiel Weintraub, Dec. 3, 1912. U. S. Pat. 1,046,043. In this process an electrical arc is utilized to effect chemical change, and to remove the reduction products from the zone in which this change is carried out.

Certain chemical compounds, as, for instance, chlorids and bromids, are to a certain extent reducible by hydrogen at high temperature, but the action is in many cases a reversible one; hence the yield of the reaction may be very small. According to this invention, the reverse reaction is prevented by the rapid removal of the reduction product from the active zone.

The process can be used in general for the reduction of chlorids and bromids which do not form solid sub-chlorids and sub-bromids, as, for instance, zirconium chlorid and boron chlorid,

and, in some cases, can also be used even when a sub-chlorid forms, as is the case with titanium chlorid.

In the use of the process applied for example, to boron chlorid, dry hydrogen is employed as a reducing agent and as a means for effecting the necessary temperature, and an electrical arc is maintained between suitable electrodes. The apparatus



is so arranged that the arc blast drives the solid reduction product, namely, boron, out of the active zone and deposits it on the walls of the apparatus and on the electrodes. This is the only solid product present; the three other substances, boron chlorid, hydrogen and hydrochloric acid, being all gaseous, are allowed to pass on to an absorbing or condensing chamber.

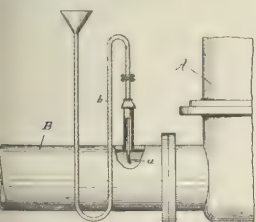
The functions of the arc in removing the solid reduction product from the heated zone will be understood by appreciating that the emanations from the cathode spot move at high velocity and start the solid reduction productions at high velocity, without doubt very much higher than that of the slow moving arc.

Ethyl Alcohol from Sulfite Liquor. Gösta Ekström, Dec. 3, 1912. U. S. Pat. 1,046,160. The patentee's improvement consists in adding urine to the waste sulfite liquor to be fermented for the production of ethyl alcohol.

Treatment of the Residual Caustic Liquor Resulting from Distillation of Wood. J. M. Neil, Dec. 10, 1912. U. S. Pat. 1,047,132. In this process caustic liquor is recovered from the residual caustic liquor by treating it with an alkali metal compound of an acid-forming metal in the presence of carbonic acid to precipitate the organic matters present. The clear liquor is then separated, treated with ozone and causticized.

Regenerating Contact Masses. W. M. Kelsey, Dec. 17, 1912. U. S. Pat. 1,047,236. In catalytic or contact processes for the manufacture of sulfuric anhydrid, the platinized contact mass, in time, loses its original efficiency in a large measure and needs to be regenerated.

In carrying out this process there is passed through the contact mass to be regenerated, a volatilized mixture of nitric acid and hydrochloric acid, at such temperature that there will be no condensation while the volatilized mixture is passing through the mass. The mixture of nitric and hydrochloric acids is conveyed through the mass either by a current of air or a current of burner gas (*i. e.*, the mixture of O_2 and air employed in the production of sulphuric anhydrid). The heat of the air or of the burner gas, as the case may be, is utilized to volatilize the mixture of nitric and hydrochloric acid employed. A temperature of $200^\circ C.$ is feasible for the purpose, but for the best results it is desirable to pre-



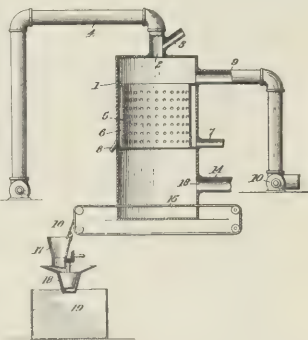
heat either the air current or the burner gas current to from $450^\circ C.$ to $500^\circ C.$, or sometimes to even a higher temperature. In practice the mixture (*e. g.*, 20 quarts of water, 2 quarts of HNO_3 , and 4 quarts of HCl) is caused to fill the funnel and trap *b*, whereupon the blower for furnishing the preheated air or burner gas to the pipe *B* is started; the whole mixture is added as fast as the small hole in the outlet of the tube *a* will permit.

Solid Compound of Nitric and Sulfuric Anhydrids. W. Schultze. Dec. 17, 1912. U. S. Pat. 1,047,576. This composition is a solid crystalline compound containing sulfuric and nitric acids, or, more precisely, their anhydrids, chemically combined together. Mixtures of sulfuric and nitric acids are largely used for "nitrating," and have hitherto been supplied to the trade in liquid form, and more or less diluted state—*i. e.*, containing water sufficient to completely hydrate at least one of the two acid anhydrids contained in the mixture.

In producing this composition sulfur trioxid gas is added to a mixture of concentrated nitric acid and concentrated sulfuric acid until a solution is formed from which crystals can be deposited upon cooling, and the composition is allowed to cool.

Treatment of Starch. Neuburger and Bergh, Dec. 17, 1912. U. S. Pat. 1,047,831. In this process starch, in a powdered form and containing moisture preferably in the amount usually

contained in green starch, is brought into contact with a body of live steam and dropped through the steam into a body of heated dry air below the steam. By this process the product is cooked in its own moisture so as to be wholly or partly gelatinized, and it is then immediately dried so as to reduce the gelatinized particles thrown down from the gelatinizing zone, thus fixing the particles in a hard, dry, gritty form. Following the drying of the particles, they are conveyed to a suitable disintegrator where they are broken to the desired degree of fineness and the starch is then ready for commercial use.



Purifying Coke. W. P. Simpson, Dec. 17, 1912. U. S. Pat. 1,047,845. In this process carbon monoxid is introduced into the retort for the purpose of eliminating sulfur and sulfurous compounds from the carbonaceous material under treatment.

Phosphoric Acid from Mineral Phosphates. F. S. Washburn, Dec. 17, 1912. U. S. Pat. 1,047,864. Mineral phosphates are ground, mixed with silica and carbon and heated to a fluid condition. The phosphorus gases driven off are mixed with air and the resulting phosphorus pentoxid dissolved in water.

Tanning Compound. J. H. McWhirter, Dec. 24, 1912. U. S. Pat. 1,047,968. Compositions containing alfalfa extract, gum gambier and sodium chlorid, singly or in mixtures.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JANUARY, 1913

ORGANIC CHEMICALS

Acetanilid.....Lb.	20 1/2 @	23
Acetic Acid (28 per cent.).....C.	2.00 @	2.15
Acetone (drums).....Lb.	16 1/2 @	17 1/2
Alcohol, grain (188 proof).....Gal.	2.55 @	2.57
Alcohol, wood (95 per cent.).....Gal.	50 @	52
Alcohol, denatured (180 proof).....Gal.	40 @	42
Amyl Acetate.....Gal.	2.65 @	2.85
Aniline Oil.....Lb.	10 1/8 @	10 9/8
Benzoic Acid.....Lb.	23 @	27
Carbon Tetrachloride (drums).....Lb.	9 1/4 @	9 3/4
Carbon Bisulfide.....Lb.	8 1/2 @	9
Chloroform.....Lb.	25 @	35
Carbolic Acid (drums).....Lb.	14 @	15
Citric Acid (domestic), crystals.....Lb.	38 1/2 @	39
Camphor (refined in bulk).....Lb.	44 @	—
Dextrine (imported potato).....Lb.	6 @	7
Dextrine (corn).....C.	2.75 @	3.06
Ether (U. S. P., 1900).....Lb.	14 @	20
Formaldehyde.....Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....Lb.	18 1/2 @	19
Oxalic Acid.....Lb.	7 7/8 @	8 1/8
Pyrogallol Acid (bulk).....Lb.	1.35 @	1.45
Salicylic Acid.....Lb.	31 @	33
Starch (corn).....C.	2.00 @	2.11
Starch (potato).....Lb.	5 1/4 @	5 3/4
Tannic Acid (commercial).....Lb.	35 @	35 1/2
Tartaric Acid crystals.....Lb.	30 1/4 @	31

INORGANIC CHEMICALS

Acetate of Lime (gray).....C.	2.50 @	2.60
Acetate of Lead (brown, broken).....Lb.	7 3/4 @	8
Alum (lump).....C.	1.75 @	2.00
Aluminum Sulfate.....C.	90 @	1.75
Ammonium Carbonate, domestic.....Lb.	8 @	8 1/2
Ammonium Chloride, gray.....Lb.	6.15 @	6 1/4
Aqua Ammonia (drums) 16°.....Lb.	2 1/4 @	2 1/2
Arsenic, white.....Lb.	4 3/4 @	5 1/4
Brimstone (crude, domestic).....Ton	22.00 @	22.50
Barium Chloride.....C.	1.65 @	1.70
Barium Nitrate.....Lb.	5 @	5 1/4
Borax, crystals (bags).....Lb.	3 3/4 @	4 1/4
Boric Acid, crystals (powd.).....Lb.	7 @	7 1/2
Bromine, bulk.....Lb.	25 @	30
Bleaching Powder (35 per cent.).....C.	1.35 @	1.50
Barytes (prime white, foreign).....Ton	18.50 @	22.50
Blue Vitriol.....Lb.	5 1/2 @	5 3/4
Calcium Chloride.....C.	65 @	90
Chalk (light precipitated).....Lb.	4 @	5
China Clay (imported).....Ton	11.50 @	18.00
Feldspar.....Ton	7.00 @	9.00
Fuller's Earth, powdered.....C.	80 @	85
Green Vitriol (bulk).....C.	55 @	60
Hydrochloric Acid (18°).....C.	1.15 @	1.55
Iodine (resublimed).....Lb.	3.05 @	3.10
Lead Nitrate.....Lb.	8 1/8 @	8 1/4
Lithium Carbonate.....Lb.	65 @	70
Magnesite (raw).....Ton	7.50 @	8.50
Nitric Acid, 36°.....Lb.	3 7/8 @	4 1/4
Phosphorus.....Lb.	35 @	90
Phosphoric Acid, sp. gr. 1.75.....Lb.	21 1/2 @	25 1/2
Plaster of Paris.....Bbl.	1.50 @	1.70
Potassium Bromide.....Lb.	35 @	37
Potassium Permanganate (bulk).....Lb.	9 1/2 @	10
Potassium Cyanide (bulk) 98-99%.....Lb.	19 @	24
Potassium Iodide (bulk).....Lb.	2.60 @	2.65
Potassium Chlorate, crystals.....Lb.	10 @	10 1/2
Potassium Nitrate (crude).....Lb.	5 @	—
Potassium Bichromate, 50°.....Lb.	6 7/8 @	7

Quicksilver, Flask.....	40.00 @	—
Salt Cake (glass-makers').....C.	55 @	65
Silver Nitrate.....Oz.	40 1/4 @	42
Soapstone in bags.....Ton	10.00 @	12.00
Sodium Acetate.....Lb.	4 1/4 @	5
Sodium Chlorate.....Lb.	8 1/4 @	9 1/4
Sodium Bicarbonate (English).....Lb.	2 3/4 @	3
Sodium Bichromate.....Lb.	5 @	5 1/8
Sodium Hydroxide, 60 per cent.....C.	1.60 @	1.65
Sodium Hyposulfite.....C.	1.30 @	1.60
Sodium Nitrate, 95 per cent., spot.....C.	2.60 @	—
Sodium Silicate (liquid).....C.	65 @	1.50
Strontium Nitrate.....Lb.	6 7/8 @	7 1/8
Sulfur, Roll.....C.	1.85 @	2.15
Sulfur, Flowers (sublimed).....C.	2.20 @	2.60
Sulfuric Acid, 60° B.....C.	85 @	1.00
Talc (American).....Ton	15.00 @	20.00
Terra Alba (American), No. 1.....C.	75 @	80
Tin Bichloride (50°).....Lb.	14 1/4 @	14 1/2
Tin Oxide.....Lb.	52 @	54
Zinc Chloride (granulated).....Lb.	4 1/4 @	4 1/2
Zinc Sulfate.....Lb.	2 1/4 @	2 1/2

OILS, WAXES, ETC.

Beeswax (pure white).....Lb.	42 @	45
Black Mineral Oil, 29 gravity.....Gal.	13 1/2 @	14
Castor Oil (No. 3).....Lb.	9 1/2 @	10 1/2
Ceresin (yellow).....Lb.	12 @	22
Corn Oil.....C.	5.80 @	5.85
Cottonseed Oil (crude), f. o. b. mill.....Gal.	37 1/2 @	38
Cylinder Oil (light, filtered).....Gal.	21 1/2 @	32
Japan Wax.....Lb.	9 1/4 @	10
Lard Oil (prime winter).....Gal.	94 @	98
Linseed Oil (double-boiled).....Gal.	44 @	—
Paraffine Oil (high viscosity).....Gal.	26 @	28
Paraffine (crude 120 & 122 m. p.).....Lb.	3 1/4 @	3 3/4
Rosin Oil (first run).....Gal.	34 @	36
Spindle Oil, No. 1.....Gal.	18 @	19
Sperm Oil (bleached winter), 38°.....Gal.	72 @	74
Stearic Acid (double-pressed).....Lb.	9 1/2 @	10 1/4
Tallow (acidless).....Gal.	65 @	68
Tar Oil (distilled).....Gal.	30 @	31

METALS

Aluminum (No. 1 ingots).....Lb.	25 3/4 @	26
Antimony (Hallet's).....Lb.	9 @	10
Bismuth (New York).....Lb.	2.10 @	2.15
Copper (electrolytic).....Lb.	16.30 @	16.40
Copper (lake).....Lb.	16 1/2 @	—
Lead, N. Y.....Lb.	4.20 @	4.30
Nickel.....Lb.	50 @	55
Platinum (refined).....Oz.	46.00 @	—
Silver.....Oz.	63 @	—
Tin.....Lb.	50 3/4 @	—
Zinc.....Lb.	7.20 @	7.30

FERTILIZER MATERIALS

Ammonium Sulfate.....C.	3.30 @	—
Fish Scrap, domestic, dried.....Unit	nominal	—
Blood, dried.....Unit	2.75 @	—
Tankage, high grade.....Unit	2.65 &	10
Bone, 4 1/2 and 50, ground, raw.....Ton	27.50 @	—
Potassium, "muriate," basis 80%.....Ton	38.55 @	—
Phosphate, acid, 16 per cent.....Ton	6.75 @	7.00
Phosphate rock; f. o. b. mine:		
Florida land pebble, 68 per cent.....Ton	3.75 @	4.00
Tennessee, 70-80 per cent.....Ton	5.00 @	5.50
Pyrites, furnace size, imported.....Unit	0.13 1/4 @	0.13 1/2
Castor meal.....Unit	nominal	—
Mowrah meal.....Ton	9.00 @	—

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V MARCH, 1913 No. 3

BOARD OF EDITORS
Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, Wm. McMurtrie, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to L. R. Hudson, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C. No claims will be allowed unless made within 60 days

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:		The Chemical Engineer and Industrial Efficiency. By W. M. Booth.	237
The Perkin Medal.		180	
The Annual Meeting at Milwaukee.		180	
The Bureau of Mines.		180	
ORIGINAL PAPERS:		PERKIN MEDAL AWARD:	
Notes on Mine Gas Problems. By George A. Burrell.		Presentation Address. By C. F. Chandler.	241
The Destructive Distillation of Sewage Sludge. By Augustus H. Fiske and Richard B. Earle.		Address of Acceptance. By James Gayley.	241
Alloys of Cobalt with Chromium and other Metals. By Elwood Haynes.		The Value of Expert Opinions. By Henry M. Howe.	246
The Relation of the Production of Alumina to the Fixation of Nitrogen. By Samuel A. Tucker.		Dr. Gayley's Interest in Education. By Edward Hart.	247
On the Relationship between the Weight of the Sugar Beet and the Composition of Its Juice. By J. Arthur Harris and Ross Aiken Gortner.		The New Age. By Rossiter W. Raymond.	249
Methods for Testing Coal Tar, and Refined Tars, Oils and Pitches. By S. R. Church.		CURRENT INDUSTRIAL NEWS:	
The Composition of Salines in Silver Peak Marsh, Nevada. By R. B. Dole, with analyses by Walton Van Winkle and A. R. Merz.		The Production of Calcium Carbide and Cyanamide in Norway.	251
Composition of the Water of Crater Lake, Oregon. By Walton Van Winkle and N. M. Finkbinder.		Potassium Salts from Seaweed.	251
Action of Fermenting Manure on Reenforcing Phosphates. By W. E. Tottingham and C. Hoffman.		The Cobalt Oxide Market.	251
The Gay-Lussac Method of Silver Determination. By Frederic P. Dewey.		The Markets for Caustic Soda and Soda Ash.	251
The Sulfo-cyanate-Permanganate Method for Copper in Ores. By D. J. Demorest.		The Preservation of Timber.	252
Electrolytic Determination of Copper in Ores, Containing Arsenic, Antimony or Bismuth. By D. J. Demorest.		Tar as a Fuel for Open-Hearth Furnaces.	252
An Electrolytic Method for the Determination of Tin in Canned Food Products. By Allerton S. Cushman and Everett B. Wettengel.		A Novelty in Gas Engines.	252
Potassium Permanganate in the Quantitative Estimation of Some Organic Compounds. By C. M. Pence.		The British Metal Trade in 1912.	252
Some Properties of Koji-Diastase. By G. Kita.		Iron and Steel Statistics for 1912.	252
Application of the Ammonium Carbonate Method for the Determination of Humus to Hawaiian Soils. By J. B. Rather.		The Production of Ammonium Sulfate in 1912.	253
LABORATORY AND PLANT:		The Petroleum Industry in the United States in 1912.	253
The New High Form of Sulfuric Acid Chamber. By F. J. Falding and W. R. Cathcart.		Conditions of the Plate Glass Industry in the United States.	253
Technical Accounting and Chemical Control in Sugar Manufacture. By David L. Davoll, Jr.		The Present Status of the Sugar Industry.	254
A Modification of the Parr Total Carbon Apparatus. By C. E. Millar.		The Production and Consumption of Rubber in 1912.	254
Improved Apparatus for Testing the Jelly-Strength of Glues. By E. C. Hulbert.		The Utilization of Blast-Furnace and Coke-Oven Gases.	254
A Useful Valve. By Nathan Smith.		Abuses in Water Filtration.	255
ADDRESSES:		The Cost of Hypochlorite Disinfection.	255
The Needs of the Mining Industry. By J. F. Call-breath.		The Paper Industry of Japan.	255
		The Gerlach Drier.	256
		Arledter's Save-All Apparatus.	256
		Uses of Cast Silicon.	257
		NOTES AND CORRESPONDENCE:	
		Notes on the Influence of the Lime-Magnesia Ratio upon Plant Growth.	257
		An Improved Method of Crude Fiber Estimation.	258
		American Mine Safety Association.	258
		The Analysis of Organic Dyestuffs.	259
		Platinum Thief.	259
		Magnesite in Lower California.	259
		Delective Artificial Silk.	260
		Increased World's Consumption of Nitrate.	260
		The Effect of Exposure on Bitumens—A Correction.	260
		The Determination of "Volatile" in Coal—A Correction.	260
		The Determination of Lime in Cow Feces—A Correction.	260
		BOOK REVIEWS:	
		Transactions of the American Ceramic Society; Preparation and Uses of White Zinc Paints; Refractories and Furnaces; The Science of Hygiene.	260
		NEW PUBLICATIONS.	263
		RECENT INVENTIONS.	264
		MARKET REPORT.	266

EDITORIALS

THE PERKIN MEDAL

Davy cautioned Faraday not to indulge in immoderate expectations of the rewards of Science. True, her gifts are not, as a rule, redundant, and they are likely, moreover, to be sometimes capriciously bestowed: but Science gives more precious rewards for excellence or success than those which can be expressed as ponderable quantities, and, among these, few are valued more highly than medals.

We look upon a medal as tangible proof of pre-eminence, for it is an indication of individual accomplishments—a token cast, in artistic mold, from a fusion of the golden opinions won by illustrious work. It furnishes the individual with evidence as to the regard in which achievements are held by his co-workers and fellow men.

On October 6, 1906, at a banquet given to Sir William Henry Perkin, at Delmonico's, New York, Dr. William H. Nichols handed to Sir William the first impression of the Perkin Medal, in gold. Dr. Nichols announced that this medal would be given annually to that chemist residing in the United States who had accomplished the most valuable work in applied chemistry during his career, whether this had proved successful at the time of execution or publication, or had subsequently become valuable in the development of industry. The Perkin Medal is therefore an acknowledgment of conspicuous services to technical chemistry—a reward for the successful application of scientific methods to industry. It is associated with the name of one of the most distinguished chemists, the founder of the immense coal-tar industry, and the recipient of the highest marks of distinction possible for Science to award; and it is conferred in order to show high appreciation of and gratitude for the success of the recipient of the medal in advancing chemical industry in one or several of its branches. In this way the applicability of chemistry to the arts and manufactures is advanced, for someone eminent in the field of chemical technology is indicated for the benefit of the aspiring technologist, and chemistry applied to the industries receives further recognition. The lessons in methods which the labors of the medalists afford must prove invaluable to all ambitious chemists.

While the award of the Perkin Medal is made by the New York Section of the Society of Chemical Industry, the largest and most prominent of the American sections of a great Society which embraces in its membership all—among the English-speaking races—that is representative of enterprise and progress in relation to the chemical arts, engineering, and industries, yet the Perkin Medal Committee, which selects the medalist, is constituted of representatives of different chemical societies of this country in addition to a representation from the Society of Chemical Industry; and, in making the selection, this Committee shows how highly it appreciates the work of the one

so honored. It is not required, as in the case of some medals, that any particular society enjoy the credit and distinction of disseminating the results of the enquiries to which his fruitful ideas give rise: the Perkin Medal is a medal of merit conferred on chemists and technologists residing in the United States for services done in technical chemistry, as determined by the scope, value and importance, and with no restrictions as to any definite field of endeavor. In being presented, therefore, with the Perkin Medal, the recipient is sensible of the great honor done him, and this sense of the honor is increased by the recollection of the eminence of the preceding medalists. Perkin, Herreshoff, Behr, Acheson, Hall, Frasch, and Gayley! How proud one must feel in being reckoned of their company!

THE ANNUAL MEETING AT MILWAUKEE

The forty-seventh annual meeting of the American Chemical Society is to be held at Milwaukee, March 25th to 28th. The general headquarters will be at the Hotel Pfister, and the meetings will be held at Marquette University, located in the business center of the city. The local committee is headed by Mr. C. H. Hall, as Chairman, and Mr. P. J. Weber, as Secretary.

The entertainment committee is planning an interesting program, and special attention is being paid to preparations for the entertainment of ladies, at such times as they cannot participate in the regular program. Many manufacturing plants will be visited. Milwaukee affords excellent opportunities to see the tanning and packing industries; the manufacture of iron and steel, engines—gasoline and kerosene, by-product coke and gas, glue, refrigerating machinery, automobiles, automobile parts and tires; shops and breweries. Most of these will be open to inspection by our members.

President Van Hise has extended a special invitation to the Society to visit the University of Wisconsin.

The plans as outlined by the local committee clearly indicate that this is to be an unusually large and successful meeting. The social, business, and scientific value of these meetings is more and more a matter of importance to the profession, and it is to the profession, therefore, that we should look for support and coöperation. Every chemist should attend at least one meeting each year. Why not begin at Milwaukee?

THE BUREAU OF MINES

The crying need of the Bureau of Mines for buildings and equipment can be easily appreciated on reading Director J. A. Holmes' Second Annual Report. The amount and value of the work already accomplished in mine safety and rescue demonstrations, fuel investigations, explosive tests and standardization, and other field work is amazing when one considers that the Bureau has never had a permanent home. It is almost inconceivable that this important department should be

housed in rented buildings. The delays and expense, already \$150,000, incident to temporary locations, seriously handicap the work.

Thirty thousand men have been killed and nearly twenty thousand seriously injured in the coal mines within the last ten years. The Bureau's work within the past year has yielded a reduction of five hundred in this annual sacrifice of life, but our losses in all mines and quarries are so greatly in excess of those in other countries as to be a very discreditable commentary on our mining methods. In the face of the wonderful results so far accomplished, the mine rescue work of the Bureau has had to be curtailed and some important phases entirely omitted, due to lack of equipment. This one branch of the Bureau's work is of sufficient

importance to merit the unlimited support of Congress.

The fact that the fuel testing done by the Bureau has saved the Government not less than \$100,000 per year during the last three years, while laboring under the most unfavorable conditions imaginable, is an indication of what can be expected if the proper working conditions are provided.

The Bureau asks for the modest appropriation of \$500,000 for buildings and proposes to use the "cheapest sort of construction that will be decent to have in a city." It wants nothing ornamental. It asks only for efficient working housing for the prosecution of its investigations, and a review of the valuable work already accomplished should serve to convince Congress of the urgent needs of the Bureau of Mines.

ORIGINAL PAPERS

NOTES ON MINE GAS PROBLEMS¹

By GEORGE A. BURRELL

The Bureau of Mines has accumulated considerable data regarding mine gases, as a result of the analysis of gas samples collected in different mines and as a result of experimental work performed in the laboratory. Some of the observations are presented here, regarding the explosibility and physiological effects of mine atmospheres, also regarding flame extinction and after-damp.

EXPLOSIBILITY OF METHANE

The limits of explosibility of methane have been worked out by different investigators and results, which in the main are in accord with each other, have been determined in the laboratory. Some differences have been published but these are mainly due to the fact that different experimenters have performed the work under different conditions. Sufficient emphasis has not always been placed upon the decided effect experimental conditions exert on the results. The size and shape of the vessel employed, nature of source of ignition, *i. e.*, whether flame, small electric spark or large electric flash; ignition of mixture from above or below; moisture in the mixture; and temperature and pressure, all may have some influence in determining the limits of explosibility of mixtures of combustible gases with air. A partial burning in a mixture of a combustible gas with air always takes place when the ignition temperature is reached, whether an explosive proportion of combustible gas be present or not. The extent of this burning will depend upon some of the conditions just referred to. But explosive limits in the sense the terms are ordinarily used have reference to those percentages of inflammable gas between which self-propagation of flame to all parts of a mixture occurs without help from the source of ignition other than the ignition of the mixture at one point. The smallest quantity of any combustible gas which when mixed with air (or oxygen) will enable

self-propagation of flame to take place is termed the lower limit of explosibility of the gas. It is of vital importance to mining men of course, that the correct limit of explosibility of methane with air be known.

LOW EXPLOSIVE LIMIT OF METHANE AIR MIXTURES

More recent work has shown that this value is about 5.50 per cent. methane and not 6 per cent. as is sometimes stated. Even 0.50 per cent. is of significance. Modern ventilation aims to keep the methane in mine air as far removed from the explosive proportion as possible. One per cent. of methane in return air is considered a large quantity. One half per cent. is sometimes tolerated. If the explosive limit for methane is 5.5 per cent. and a mining management calls 6 per cent. the low limit of explosibility, they are 0.5 per cent. nearer the explosive proportion than they think.

Coquillon ignited methane-air mixtures in a closed vessel by means of an electric spark, and placed the lower limit of explosibility at 5.8 per cent. methane. Le Chatelier and Mallard and Boudouard have placed the limit at 6.0 per cent. Eitner determined the lower limit of explosibility of methane to be 6.1 per cent. Clowes obtained 5.0 per cent. as the low limit of explosibility when the gas was fired from below with a flame and 6.0 per cent. as the limit when the gas was fired from above. Teclu found the lower limit of explosibility to be between 3.20 and 3.67 per cent. Teclu's values are quite outside of the others mentioned here. The most recent values are those obtained by Burgess and Wheeler who place the lower limit of explosibility between 5.5 and 5.7 per cent. No discussion of the different methods of experimentation will be given here, the object being only to convey the idea that exact duplication of results by different experimenters has not always followed.

In the Bureau's laboratory an explosion could not be obtained when a mixture of methane and air containing less than 5.5 per cent. methane was subjected to the action of a small $\frac{1}{8}$ inch spark from an induction coil. The latter was driven by four dry cells. The mixture was placed in a 100 cc. spherical vessel over

¹ Presented by permission of the Director of the Bureau of Mines at the winter meeting of the West Virginia Coal Mining Institute, Parkersburg, W. Va., December, 1912.

mercury. An explosion could not be obtained with 0.1 per cent. less methane when the pressure was increased from one atmosphere to two atmospheres. With 5.50 per cent. of methane, combustion was not quite complete. Analysis of the products of combustion showed, however, that only a trace of combustible gas remained unburnt. Pure methane was prepared by the action of alcohol and methyl iodide on a zinc-copper couple.

A number of experiments have been performed in the Bureau's laboratory in which a flame has been used as the source of ignition. In some of those experiments a spherical flask having a capacity of one liter has been used. Some burning followed under these conditions when as little as 4.75 per cent. methane was present. Ignition was effected from below. The burning extended as a cone about one-half of the way to the top of the flask. Inflammation in the mixture increased with increasing percentages of methane. All mining men have of course noticed this behavior in mixtures of combustible gases and air. With very small percentages the inflammation starts as a cap on the flame of the safety lamp. The inflammation spreads from the source of ignition as the percentage of combustible gas is increased. Finally conditions are right for a projection of flame throughout the mixture. At about 5.50 per cent. the low limit of explosibility, the flame extends to all parts of the mixture but travels comparatively slowly and can be followed by the eye. With increasing proportions of methane, the explosion becomes more violent. It was observed that the partial burning in a mixture containing less than 5.50 per cent. methane depended upon the several factors such as nature of ignition, shape of container, etc., but that complete explosion could not be obtained under several different conditions of experiment tried when less than 5.5 per cent. of methane was present. In determining the low explosive limit of methane-air mixtures, the products of combustion were examined to ascertain the completeness of the combustion. In the experiments that follow, this was not done unless otherwise stated. The term explosion will be retained to mean conditions when the flame filled the container as far as could be seen by the eye. Inflammation will mean only a partial filling of the container by the flash. The foregoing remarks are preliminary to a brief account of some experiments regarding explosibility of fire-damp, which are not so well known.

EFFECT OF CARBON DIOXIDE ON THE EXPLOSIBILITY OF METHANE

In explosions, as well as flame extinction and physiological effects, the influence of carbon dioxide in mine air has usually been overestimated. Carbon dioxide always occurs in mine gas mixtures in which explosive amounts of methane are present and there is always a greater oxygen deficiency than is produced when the methane is added to air for simple laboratory experiments. The following experiments show something about the explosibility of methane in the presence of excessive proportions of carbon dioxide and when the oxygen is considerably reduced.

In the Bureau's laboratory, when 2.5 per cent. of carbon dioxide was present in a mixture, an explosion followed when the methane was raised to 5.83 per cent.

With 5.0 per cent. carbon dioxide an explosion occurred when the methane was raised to 6.25 per cent. With 10.0 per cent. of carbon dioxide an explosion was obtained when the methane constituted 6.6 per cent. of the total. A small spark from an induction coil was the source of ignition. The presence of carbon dioxide narrows the explosive limits but it will be observed that even 10 per cent. only raised the low limit to 6.60 per cent.

EFFECT OF REDUCED OXYGEN ON THE EXPLOSIBILITY OF FIRE-DAMP

A spherical flask having a capacity of 1 liter was used in the following experiments: A mixture of the following composition was experimented with:

	Per cent.
Carbon dioxide.....	0.03
Oxygen.....	14.00
Methane.....	9.40
Nitrogen.....	76.57

When this mixture was exposed to a flame from above inflammation occurred. The flame spread downward to the middle of the flask, and out toward the sides where it died. The eye could easily follow the course of the wave. When the mixture was ignited with a flame from below, it exploded with considerable force. As far as the eye could see the flame filled the entire flask.

Further experiments were made in which the oxygen had been reduced to 13 per cent. This mixture had the following composition:

	Per cent.
Carbon dioxide.....	0.03
Oxygen.....	13.00
Methane.....	9.40
Nitrogen.....	77.57

The mixture was placed in a cylindrical vessel having a capacity of 2750 cc. Two copper terminals were quickly broken to produce the flash, which took place in the center of the vessel. A current of 7.5 amperes at a pressure of 220 volts was used. A flash about one-half inch long could be obtained. On the break of the contact the inflammation spread upward almost to the top of the jar.

With 15.1 per cent. oxygen and 9.4 per cent. methane, a quite violent explosion was obtained under the same conditions of experimentation. Experiments were also performed in which a small one-eighth inch spark from an induction coil was used as the source of ignition. A mixture having the following composition exploded:

	Per cent.
Carbon dioxide.....	3.92
Oxygen.....	16.25
Methane.....	9.43
Nitrogen.....	70.37

Under the same conditions a mixture having the following composition in which the oxygen was slightly diminished, did not inflame at all:

	Per cent.
Carbon dioxide.....	3.99
Oxygen.....	15.90
Methane.....	9.25
Nitrogen.....	70.86

It was observed in conducting these explosibility experiments that both the electric flash and flame produced inflammation under more severe conditions than the small spark; also, a flame when applied from below will produce inflammation, under more severe conditions, than when applied from above.

These are only a few of many experiments which have been made on the explosibility of gaseous mixtures at the Bureau's laboratory. Some experiments have been made in which black powder has been fired into mixtures of gas and air, in a gallery having a capacity of 600 cubic feet.

Much interest and criticism has followed Dr. John Harger's (England) proposal that the oxygen be decreased and carbon dioxide be increased in mines to prevent explosions. Briefly, Dr. Harger's proposition is this: A small reduction in the oxygen percentage and a small increase in the carbon dioxide percentage in mine air will suffice to produce an atmosphere incapable of supporting combustion and consequently an atmosphere in which explosions and gob fires cannot occur. For average mines it is suggested to start the experimental work on a large scale; that the oxygen should be reduced to 20 per cent. (*i. e.*, 1 per cent. below normal) and a half per cent. CO_2 added to it. Where the conditions were more dangerous the oxygen should be further reduced, say, to 19 per cent., and the CO_2 increased to three-quarters of 1 per cent.

Time will not be devoted now to a discussion of the many points involved in Dr. Harger's suggestion, unless it is the wish of the Institute. Experiments which have been performed by the Bureau, some of which are here presented, indicate that the oxygen percentage will have to be reduced much below the figures mentioned by Dr. Harger to prevent all explosions. Of course, as the oxygen percentage is decreased the mixture explodes less violently and less completely. As regards carbon dioxide, so much would have to be added to prevent fire-damp explosions that it appears that its use for that purpose would be entirely precluded.

MINE-GAS MIXTURES CONTAINING EXPLOSIVE AND OTHER PROPORTIONS OF METHANE

Below are given some analyses of mine-gas samples, some of which contain explosive proportions of methane. The accompanying carbon dioxide and oxygen content are of interest in connection with foregoing experiments. The samples were collected in mines wherein ventilation had been interrupted for some time. Explosions had occurred in these mines.

Sample number	CO_2	O_2	CH_4	N_2
1.....	8.28	10.50	4.49	76.73
2.....	0.48	17.49	9.20	72.83
3.....	5.81	13.95	5.07	75.17
4.....	1.75	17.63	7.60	73.02
5.....	0.34	19.46	5.79	74.41
6.....	0.35	18.81	7.25	73.59
7.....	2.00	15.64	7.37	74.99

Samples Nos. 2, 4, 5, 6 and 7 are explosive. There could be but very slight inflammation in mixtures represented by samples Nos. 1 and 3.

Knowledge of the explosibility of mixtures as they occur in mines has been especially useful to the Bureau in that such atmospheres are frequently encountered in exploration work following mine explosions and fires.

EXTINCTION OF ACETYLENE FLAME

The Bureau has already called attention to the tenacity to existence of the acetylene flame, in that it will exist in atmospheres in which the ordinary wick-fed flame is extinguished. It was found that a residual atmosphere in which an acetylene flame had been extinguished contained 11.70 per cent. oxygen and 6.30 per cent. carbon dioxide. More recent experiments have confirmed this finding. It was also found that when about one-half of the carbon dioxide was removed as it was formed the acetylene flame burned in a slightly greater oxygen deficiency. For these experiments the flame was placed in a gas-tight cabinet, having a capacity of 25 cubic feet. The residual atmosphere after the flame had been extinguished had the following decomposition:

	Sample from middle of chamber	Sample from bottom of chamber
Carbon dioxide.....	3.22	3.17
Oxygen.....	10.99	11.12

The Bureau has observed that in mines when the oxygen has decreased to 11 per cent., about 6 per cent. of carbon dioxide on the average will be present. An objection has been raised to the use of the acetylene flame in that it becomes extinguished only when there may be grave danger to men, because of the presence of much black damp. The acetylene flame, as is the case with other flames, burns less brightly as the proportions of oxygen in mine air diminishes. It was observed at the Bureau's laboratory that when the oxygen content of air decreased to about 16 or 16.5 per cent. the flame resembled the ordinary wick-fed flame when the latter burns in pure air, *i. e.*, air containing 21 per cent. oxygen. This indication can be used as a guide against men venturing into black-damp workings containing less oxygen than this proportion.

EFFECT OF CARBON DIOXIDE ON THE EXTINGUISHMENT OF THE FLAMES OF MINERS' LAMPS

The ordinary miners' lamp is extinguished when the oxygen falls to about 16.5 or 17 per cent. This extinguishment is almost entirely due to the oxygen deficiency and not to the carbon dioxide, since this constituent is rarely ever present in sufficient quantity when the oxygen in mine air drops to 16 or 17 per cent., to exert any appreciable effect. When a lighted candle was placed in a bell jar filled with ordinary air it went out when the oxygen percentage fell to 16.24 per cent. The carbon dioxide produced by the burning amounted to 2.95 per cent. When 3.22 per cent. of carbon dioxide was originally in the air the atmosphere, after the extinguishment of the flame, contained 16.68 per cent. When the atmosphere

originally contained 13.52 per cent. carbon dioxide and 20.67 per cent. oxygen the flame went out when the oxygen had fallen to 17.39 per cent. These analyses are tabulated below:

	Composition of atmosphere at beginning of experiment		Composition of atmosphere in which flame went out	
	CO ₂	O ₂	CO ₂	O ₂
1.....	0.04	21.00	2.95	16.34
2.....	3.22	21.13	6.51	16.68
3.....	13.52	20.67	16.00	17.39

It will be observed that the initial presence of a large amount of carbon dioxide had little effect on the flame extinguishment. In all of these laboratory experiments the flame probably existed a trifle longer than would be the case in actual mining practice, because in mines a slight gust of air or sharp thrust of a lamp would puff out a diminishing flame.

EFFECT OF VITIATED AIR ON THE LUMINOSITY OF MINERS' LAMPS

J. S. Haldane¹ recently made an important contribution to mining literature when he determined the effect on the light of a safety lamp when burned in atmospheres deficient in oxygen. Mine air is always deficient in oxygen to some extent as compared with outside air. This deficiency may amount to from 0.1 to 0.2 per cent., to 2 or more per cent. under ordinary working conditions.

A table which J. S. Haldane prepared is of exceptional interest and is here presented:

OBSERVED PERCENTAGE DIMINUTION OF LIGHT WITH OBSERVED PERCENTAGE DIMINUTION OF OXYGEN

Light given	Oxygen percentage	Light percentage diminished	Oxygen percentage diminished
100	20.93	0	0.00
90	20.66	10	0.27
77	20.34	23	0.59
66	19.88	34	1.05
41	19.34	59	1.89
27	18.92	73	2.01
11	18.28	89	2.65
0	18.01	100	2.92

Dr. Haldane observed, roughly speaking, that every diminution of 0.1 per cent. in the oxygen caused a diminution of 3.5 per cent. of the value of the light in the pure air.

HIGH VELOCITY OF AIR CURRENTS IN MINES

As against many good reasons put forth for keeping miners plentifully supplied with fresh air, there has arisen the protest that with high velocities of air currents in mines and high oxygen content of mine air, explosions have increased in number. Low oxygen content as a preventive of explosions has been discussed in part in this paper; the question of high velocities is more completely wrapped up with the question of dust explosions, and will not be discussed here.

AFTER-DAMP

Two samples of after-damp atmospheres are here presented. They are of interest as showing the large amount of carbon monoxide (white-damp) present shortly after an explosion.

Sample No. 1 was collected 30 minutes after an explosion had occurred at the Experimental mine

of the Bureau at Bruceton, Pa. It was taken in the main entry at the junction with the first right butt entry after ventilation had been restored in the main entry.

Sample No. 2 was collected at the face of the first right butt entry 100 feet from where Sample No. 1 had been collected. Ventilation had not been restored in this entry.

	Sample No. 1	Sample No. 2
Carbon dioxide.....	0.26	1.54
Oxygen.....	20.26	17.79
Carbon monoxide....	0.16	1.89
Methane.....	0.12	0.65
Nitrogen.....	79.20	78.13
Hydrogen present less than 0.20 per cent.		

These analyses are instructive as showing that very dangerous atmospheres may exist after an explosion in a mine in close proximity to atmospheres wherein men would not soon feel distress. The Bureau found that in 0.16 per cent. carbon monoxide a mouse shows only slight signs of weakness at the end of one hour's time. In the same atmosphere a bird showed signs of distress in 3 minutes time and fell from its perch in 18 minutes.

In exploring a mine containing after-damp a person could, by disregarding the warning of a sensitive animal like a canary, travel in a very short time from an atmosphere that would not distress him rapidly into one where collapse would quickly follow.

AUTOMATIC GAS SAMPLER

The Bureau has lately developed an automatic mine gas sampler to a stage of completion where it is believed samples of after-gases can be trapped at the time an explosive wave goes by and at prearranged intervals thereafter in order that the chemistry of the explosions in the Experimental mine may be better studied.

An analysis of a sample collected at the Altoft Experimental station (England) $\frac{1}{20}$ of a second after the explosion had passed contained the following constituents:

	Percentages
Carbon dioxide.....	11.25
Oxygen.....	1.15
Carbon monoxide.....	8.15
Hydrogen.....	2.75
Methane.....	2.95
Nitrogen.....	73.75

The high percentage of carbon monoxide will be noticed. The British report calls attention to the presence of oxygen as showing the inrush of air even so short a time after the explosion wave had passed. They state that, at the instant of passage of the flame, the oxygen should have been entirely consumed. The gallery at Altoft's is above ground, however, and inrush of pure air would be quicker than in a mine.

DISTRIBUTION OF AFTER-DAMP

It is well known to mining men that after an explosion, parts of a mine may be quite unaffected by the explosion, and that in some places the products of the explosion (white-damp, etc.) may not penetrate. Men have lived for days in some mines after explosions until rescued. On the other hand, men rushing into the track of the explosion in the dash for safety have

¹ Colliery Guardian, October 25, 1912.

frequently been overcome. As is generally recognized, the heaviest toll of life is almost invariably due to the white-damp and not to explosive violence.

USE OF BIRDS FOR CONTINUED EXPLORATION WORK

The Bureau has made experiments having to do with the use of canaries for continued exploration work, having in mind the fact that the same animal might be used and overcome several times in the same day. It was found that even after repeated exposures to carbon monoxide these animals, upon subsequent exposures, show distress, collapse and revive in about the same period of time as on the first exposure. Consequently these animals can be used again and again for all practical purposes with the knowledge that they will not be less efficient for exploration work even after repeated exposures. No parallel can be drawn regarding the effects on men of carbon monoxide from these experiments. Men have been months recovering from severe cases of poisoning, and the after-effects have been very formidable. To show how differently carbon monoxide affects men and animals the following experiments performed by the Bureau are here tabulated:

QUANTITY OF CO USED = 0.25 PER CENT.			
Effects on Canaries			
Time exposed 3 minutes	Distress 2 minutes	Collapse 3 minutes	Recovery 7 minutes
Effects on Mice			
Time exposed 12 minutes	Distress 6 minutes	Collapse 12 minutes	Recovery 25 minutes
Effect on Man			
Time exposed 20 minutes	Distress 1 hour	Collapse	Recovery 8 hours

Whereas the animals were left in the atmospheres until they collapsed, the man left the atmosphere experiencing but little discomfort at the end of 20 minutes. One hour later he became very sick. Much might be written about the poisonous action of carbon monoxide. A further discussion will be reserved for a Bureau publication.

USE OF SPARROWS FOR RECOVERY WORK

The Bureau has attempted to use English sparrows for recovery work in mines with not much success, because those so far obtained have not survived captivity. Pigeons are not sensitive enough. At the end of 11 minutes in an atmosphere containing 0.25 per cent. of carbon monoxide, they showed but slight signs of distress. Mice are more sluggish and not so easily affected as canaries, but at the same time, useful. A mouse and a canary together would make a good combination. The usefulness of small animals for detecting bad air in mines has been so well recognized in England that they are kept at all mine safety stations and some collieries. The Bureau of Mines of this country keeps them at all of its stations.

INTRUSION OF NATURAL GAS INTO COAL MINES

Natural gas has intruded into some coal mines with disastrous consequences. Mining men are alert to the importance of the questions. Old abandoned wells are an especial menace in that nobody knows the whereabouts of some of them.

Some comparison between the explosibility of natural gas and fire-damp is interesting. Natural gases of the Appalachian fields contain other paraffin hydrocarbons than methane, principally ethane. The following analysis shows the composition of the natural gas used at Pittsburgh. This gas is drawn largely from West Virginia. Some comes from Western Pennsylvania.

Carbon dioxide.....	trace (less than 0.10 per cent.)
Oxygen.....	0.00
Methane.....	82.5
Ethane.....	16.0
Nitrogen.....	1.5

Carbon monoxide, hydrogen or ethylene are not contained in the gas, not even in traces.

Below are shown the explosive limits of methane-air mixtures, and natural gas-air mixtures. Ignition was effected by a small electric spark from an induction coil.

	Methane	Natural gas
Low limit.....	5.50	4.92
High limit.....	12.50	12.00

Below are given the ignition temperatures of methane and ethane, determined by Dixon and Coward:¹

Methane.....	650°-750° C.
Ethane.....	520°-630° C.

It does not appear from the above that natural gas is so much more sensitive to inflammation as to produce an added menace from this cause upon intrusion into a mine. The great danger lies in the sudden inrush of a large body of inflammable gas which has not always been controlled in order to every disaster. The fact that carbon monoxide is not present in the gas is fortunate. Many published analyses show natural gas to contain this constituent. The statement is erroneous. Higher paraffin hydrocarbons than methane in natural gas give to the latter its characteristic odour.

INFLAMMABLE CHARACTER OF THE GASES PRESENT IN MINE AIR

The Bureau has almost ready for publication a report showing the exact character of the inflammable gases present in many samples of mine air. In many text books, the statement is made that hydrogen, ethylene, carbon monoxide, and ethane may be present in mine air under normal conditions of operation; as far as the authors of these books are concerned, they have been justified because occasionally analyses showing these constituents are reported, although, even so, the bulk of evidence shows them to be of rare occurrence under the conditions cited. Because of the reported presence of these gases in mine air the question has, at times, been raised regarding the application to mining conditions of experiments performed in the laboratory or testing galleries, in which methane or the nearly similar natural gas is used. In the Bureau's report, mine gas samples from about 50 mines are listed. Methods of examination are described. The great effect of very small errors which can hardly be avoided in the manipulation of many forms of gas analysis apparatus is shown in that these

¹ Chem. News, 99, 139 (1909).

small errors may result in the reporting of one or more per cent. of combustible gases other than methane. Of course, if a careful analyst reports other combustible gases than methane in even a few samples, then one is justified in believing that they may occur in other samples. The above statement excepts a few mines around the oil regions into which natural gas may have escaped.

A rather complete bulletin is also ready having to do with methods of examination of mine and natural gases. Apparatus is shown for research work, also simple machines that can be easily operated at mines. Chemical analyses are the basis from which safety lamps and other gas indicators are constructed and simple methods for these standard tests are desired. An abstract from the larger bulletin has also been completed which contains only those chemical apparatus suitable for use at mines.

USE OF BIRDS AND MICE FOR EXPLORATION PURPOSES

A publication has also been prepared containing further work regarding the use of canaries and mice. A short abstract of these findings is given in the preceding pages.

COÖPERATIVE WORK WITH ILLINOIS

In coöperation with the State of Illinois a large number of samples have been collected in that state by N. H. Darton, Geologist of the Bureau. This has also been done in the anthracite fields of Pennsylvania. The results of analyses of these samples are being shaped into a report, and will show the composition of the air in many different mines in those states. Mr. Darton also reports interesting findings having to do with geological conditions and methane liberation.

NORMAL MINE AIR SAMPLES

In conjunction with G. S. Rice, Chief Mining Engineer of the Bureau, a preliminary report is being assembled showing the composition of the mine air in many different coal mines, under normal conditions in different parts of the country. Almost all of the data has been assembled for this work.

MINE GASES AND EXPLOSIONS

Mine gas samples have also been collected by mining engineers of the Bureau following many mine explosions. Their significance will be discussed in the reports of those explosions.

USE OF GASOLINE LOCOMOTIVES

A large number of samples were collected having to do with use of gasoline motors in mines.

Exhaust samples have been collected, also samples of the air in the mines where motors were operated. Special investigations have been made for coal operators, inspectors, and motor manufacturers at their request. It seemed best to defer a report for publication, however, until results could be obtained connecting exhaust gases with power developed, gasoline consumption different carbureter arrangement, etc. This work is in progress and is under the direction of O. P. Hood, Chief Mechanical Engineer of the Bureau.

BLACK-DAMP IN MINE AIR

Enough data has also been collected for the issuance

of a publication on black-damp in American mines. Also one on after-damp.

MINERS' CIRCULAR

A miners' circular is being prepared, having to do with a discussion of mine gases. No attempt, of course, is being made to replace those mine gas terms, with which miners are most familiar, such as black-damp, after-damp, after-gases, fire-damp, etc., but a circular showing the Bureau's observations on these subjects will be published, since in the performance of investigative work these names must, at times, be replaced by the chemical ones. Black-damp is still sometimes wrongfully used as meaning carbon dioxide instead of a mixture of nitrogen and carbon dioxide. The latter usually plays but a small part in the combustion effects produced by the mixture.

The deficiency of oxygen, which always accompanies excessive proportions of black-damp, is the main factor in flame extinguishment in mines. On the other hand, physiological effects, if produced in men when they are in atmospheres in which lamps do not burn, are frequently due to the carbon dioxide. This statement has reference to atmospheres in old workings, etc., and not those that have been vitiated by mine fires, explosions, etc., and wherein carbon monoxide might exist. Different meanings have been attributed to the word "fire-damp." To some it means methane, to others any mixture of methane and air. That other gases than methane may frequently be present is sometimes stated. Some persons define it as any inflammable mixture of methane and air.

Sufficient data are not at hand to completely describe the constituents present in after-damp. That the products of incomplete combustion of methane, coal dust and air can be quite complex, is shown by work already performed on single gases and air. This statement has reference to the immediate after-products of an explosion. The Bureau hopes to secure data on this point at the experimental mine.

After a stagnant mine atmosphere has been clarified of smoke particles and easily soluble gases, and gases that irritate, there can remain, for a long time, a clear atmosphere containing oxygen, carbon dioxide, nitrogen, methane, hydrogen and carbon monoxide; an atmosphere with only the characteristic odor of burnt coal and wood, yet one that can be fatal because of the presence of the carbon monoxide. Oxygen may be present in sufficient quantity to enable a lamp flame to burn fairly well, and absolutely no indication given to an exploring party of the presence of carbon monoxide, although the latter may be present in sufficient amount to produce fatal results. Deaths have been caused by men relying upon the lamp flame to warn them of carbon monoxide.

BUREAU OF MINES
PITTSBURGH

THE DESTRUCTIVE DISTILLATION OF SEWAGE SLUDGE

By AUGUSTUS H. FISKE AND RICHARD B. EARLE

Received November 29, 1912

HISTORICAL

The problem of utilizing sewage sludge divides itself.

naturally into two divisions: First, the elimination of moisture, and second, the disposal of the solid material most advantageously. Experiments leading to the solution of these problems are constantly being tried, and in different places varying methods are in use. In England, filter presses and rotary driers, and in Germany, besides these, centrifugal driers have also been employed to bring the moisture in the sludge down to 60–80 per cent. Ruggles¹ estimates the cost of drying sludge to a moisture content of 8–10 per cent. at \$1.66 per ton. This material is then sold as fertilizer. It is estimated² from analyses of the fertilizing constituents, that the substance should be worth \$7.50 to \$10.00 per ton, but it seems probable that the reason it has not come into wider use for this purpose is the fact that it contains grease.

Schweitzer³ states that at the city of Elbing, the sludge contains 60–70 per cent. of water when it leaves the filter presses. It is then allowed to remain two to four weeks in the open, and then, either used for fertilizer (containing 2–4 per cent. nitrogen), or burnt in a suction gas producer. At Hannover⁴ where centrifugal driers are employed, the sludge contains 50–70 per cent. of water, a slight improvement over the filter presses. In experiments at Brunn,⁵ Austria, a rotary drier, heated artificially, was used, and the content of moisture in the sludge reduced to 25 per cent. before being utilized for the preparation of illuminating gas. For this purpose, 100 kg. of the sludge were mixed with 2 kg. of coal, and on distilling the mixture 23 cu. m. of gas were obtained per 100 kg. sludge.

Bayer and Fabre⁶ gave the mean of 75 analyses of sludge as follows:

	Per cent.
C.....	31.04
H.....	3.95
N.....	2.87
O.....	20.73
Ash.....	41.41
P ₂ O ₅	1.03
K.....	0.42

In their experiments 55 kg. of sludge were distilled at a time, the distillation lasting 2½ hours, and the yield of gas was on a basis of 23.8 cu. m. gas per 100 kg. sludge. At Frankfort,⁷ dried sludge used in a gas producer yielded 20 cu. m. gas per 100 kg. of dry sludge.

In England, Purcell⁸ distilled dry sludge and obtained ammonia and gas. He also states that the residue from the distillation is valuable to the cement manufacturer. At Chorley,⁹ illuminating gas is made in small amounts from the sludge. At Manchester, and Kingston-on-Thames, the sludge is dried and sold as fertilizer. At Norwich, grease is recovered from it. At Leeds a small plant for destructive distillation of

the sludge has been used for the purpose of recovering ammonia. At Oldham, grease is recovered by treating the sludge in a retort with steam.

DESCRIPTIVE

The following experiments were tried with sewage sludge from the precipitation plant at Worcester, Massachusetts, where the treatment of the sewage is essentially as follows: Milk of lime is first added to crude sewage and the mixture run into large tanks to settle. The crude sewage contains large quantities of soluble iron salts, due to the iron works in the city. The lime precipitates the iron compounds which carry down with them most of the solid material in the sewage. After settling, the clear effluent is drawn off, and the dilute sludge pumped to filter presses, where its moisture content is reduced to about 75 per cent. It is then dumped away. The sludge from the press is a dark chocolate brown substance of a claylike consistency and sp. gr. about 1.2. It comes from the press in sheets about ¾ inch thick, which give a faint, rather unpleasant odor. The average content of water was found to be 72 per cent.

Experiments on the drying of this substance were tried, and it was found that it dried readily in a current of warm air leaving a brown friable residue of a sp. gr. 0.3. If the temperature was maintained about 70°–80° C., it dried in less than 10 hours. If the substance was merely exposed to the air of the room, about 16° C., it required four days for the substance to lose all but about 10 per cent. of its moisture, and thereafter the drying process was very slow.

The dried substance was next subjected to destructive distillation by two methods. In the first series of experiments, the dry sludge was distilled in a small iron retort directly connected to a condenser and suitable gas washing bottle. In the second series, the retort was connected directly with a coil of ½ inch gas pipe about 2½ m. long kept at a red heat, through which the products of distillation passed. The rest of the apparatus was essentially the same in both series. One of the gas washing bottles contained a dilute solution of sulfuric acid to absorb any ammonia which might be evolved.

In every experiment the retort was heated to a bright red, and kept in this condition until the evolution of gas was less than thirty bubbles per minute, experiments having shown that the distillation was practically complete when this condition had been reached. It was then allowed to cool, and on opening, it contained a black, friable charcoal weighing about 58 per cent. of the original sludge. This substance contained 18.8 per cent. of carbon, and the ash from burning it, contained Fe and Ca, as bases, and Cl, PO₄, SO₄, CO₃, as acids.

In the first series, where the red hot coil was not used, the liquid distillate was a brown oil smelling of pyridine bases and weighing about 20 per cent. of the weight of the original sludge. It was subjected to fractional distillation with the following results: 59 per cent. of the oil collected in the fraction up to 100° C., 17 per cent. at 100° to 115° C.; 10 per cent. at 240° to 285° C.; black tarry residue 13 per cent. left

¹ Eng. Record, 63, 79.

² Ibid., 65, 701.

³ J. Gasbel, 54, 231.

⁴ Eng. Record, 58, 445.

⁵ Rev. chim. Ind., 21, 779.

⁶ Rev. gén. chim., 14, 199.

⁷ Eng. Record, 58, 445.

⁸ Trans. Inst. Min. Eng., [4] 35, 37; Brit. Pat., 18,199, Aug. 31, 1908.

⁹ Mun. J. Eng., 32, 483.

in still. A few qualitative tests on these fractions showed thiophene, pyrrol, and possibly indol. In the second series, where the products of distillation passed through the red hot coil, the liquid distillate was only about $\frac{2}{3}$ of the amount collected in the first series. It was black, and had the odor of ordinary gas works tar, probably containing similar constituents.

The evolution of gas in the first series, was on the basis of about 11.38 cu. m. per 100 kg. dry sludge. When burned in a fishtail burner, it gave a flame containing a comparatively large proportion of blue, and was distinctly poor in illuminating constituents.

In the second series the yield of gas was on a basis of 19.08 cu. m. per 100 kg. dry sludge, and was far superior in illuminating qualities, not only to the gas made in the first series, but also to the gas from the city main.

The following table is a comparison of the results obtained with the Worcester sludge and those of Bayer and Fabre, and others:

	Worcester sludge by direct distillation	Worcester sludge distilled with use of red hot coil	(Frankfort) 20 cu. m. (common gas coal) 0.13 kg. to 0.28 kg.	Bayer and Fabre 23.8 cu. m. 0.75 kg.
Gas per 100 kg. . .	11.4 cu. m.	19.1 cu. m.		
NH ₃ per 100 kg.	0.27 kg.		
Tar.....	20%	13%	3%	
Organic matter in sludge.....	50%		60%
Yield of coke.....	58.3%	60%	57.6%
Carbon in coke..	18.5%	90%	

Composition of gas evolved:

	CO ₂	C ₂ H ₄ , etc.	O ₂	CO	CH ₄	H ₂	N ₂	Sp. gr.
Worcester sludge:								
First series.....	24.6	5.0	0.6	9.6	13.9	18.8	27.8	0.733
Second series.....	18.4	15.9	0.7	7.5	13.8	28.2	15.5	0.499
Bayer and Fabre:								
1907.....	2.2	4.8	0.8	17.5	18.1	44.2	12.0
1908.....	2.2	7.3	0.8	14.4	23.2	41.7	7.9
Coal gas (a).....	1.1-1.8	3-5.7	...	3-9	32-39	42-53	1.0-5.0	0.468

(a) "Gas Manufacture," by W. J. A. Butterfield, p. 76.

EXPERIMENTAL PORTION

To dry the sludge, two methods were tried, at the temperature of the room, and over a steam radiator where there was a good circulation of air. The temperature of the room was about 16° C., while the air above the radiator varied from 60°-80° C. The following figures are typical of many series of drying experiments:

	Original weight	After 10 hrs.	After 24 hrs.
At room temperature....	264 grams	207 grams	155 grams
On radiator.....	172 grams	67 grams	65 grams
	After 48 hrs.	After 72 hrs.	After 12 days
At room temperature....	106 grams	92 grams	84 grams
On radiator.....	No further loss		

Thus we see that the sludge on the radiator was practically dry in 10 hours, while the sludge at the room temperature lost 21 per cent. of its moisture in that time. After 24 hours it had lost 41 per cent., the next day 60 per cent., the following day 65 per cent., and thereafter the loss was very slow, its moisture content being reduced to about 3 per cent. at the end

of 12 days. In each case the sludge was in the form of the filter press sheet.

The dry substance was light brown in color and almost odorless. It was found to contain approximately 50 per cent. of organic matter, while the sludge used by Bayer and Fabre¹ contained almost 60 per cent. This partly explains the smaller yield of gas from the Worcester sludge. When burnt to an ash, a brownish residue was left, the color being apparently due to iron. It had a strong alkaline reaction and contained phosphates, sulfates, chlorides, carbonates, calcium, iron and small amounts of the alkali metals. A quantitative analysis was not made, but it is probable that it contained about 1 per cent. of phosphoric acid and less than 0.5 per cent. of potassium, the results of Bayer and Fabre.

The dry sludge was heated in a small iron retort, 60 grams being taken for each charge. This yielded an average of 35 grams of a black friable residue containing 18-19 per cent. of carbon. In the first series of experiments, where the superheating coil was omitted, a brown oil was collected from the condenser, which had an odor resembling the tar of an old tobacco pipe. It averaged in weight 20 per cent. of the weight of the original charge of sludge. When fractionally distilled the following results were obtained:

Weight of oil taken 97 grams
 Fraction (a) to 100° C. 57 grams
 Fraction (b) 100-115° C. 17 grams
 Fraction (c) 115-135° C. a few drops
 Fraction (d) 135-240° C. nothing
 Fraction (e) 240-285° C. 10 grams
 Residue in still, 12 grams

There was a distinct break in the continuity of the distillation between 115 and 240°, and another between 265 and 284°. At this latter point much of the oil in the last fraction was distilled. The temperature then fell to 220°, whereupon the distillation was stopped. A thick, black tar remained in the still which would not distil with steam, and was not investigated further. Anderson² states that in the distillation of bone oil there was a break in the distillation after $\frac{2}{3}$ of the oil had been distilled. This is like the break in the distillation of the sludge oil already described. He states that the temperature had to be considerably raised in order that the distillation might continue uniformly. No thermometric data are given.

A few qualitative tests on the fractions were made in order to get a general idea of their composition. Fraction (a) contained water, ammonia, gave a deep red with sulfuric acid, probably thiophene, and turned a pine shaving deep red, probably pyrrol. Fraction (b) was composed of two layers. The lower contained water and pyridine, the latter shown by a test with hydrochloric acid and chlorplatinic acid which gave a red insoluble precipitate. The upper layer was mostly pyrrol as its vapors colored a pine shaving moistened with hydrochloric acid a deep red. Fraction (c) gave no definite tests though indol was indicated by the action of NaNO₂ and H₂SO₄.

The gas which was freely evolved during distillation

¹ Trans. Royal Soc. Ed., 16, 463.

measured 6-7.5 liters per charge of 60 grams of sludge, or on a basis of 11.38 cu. m. per 100 kg. It was collected over water and allowed to stand over night. It was then burnt in a fishtail burner and found to give about $\frac{1}{2}$ the illumination that the city gas supply gave. The flame contained a comparatively large porportion of blue. Analysis of the gas gave the following results, 100 cc. being taken for each analysis and the analyses being done in duplicate:

Vol. after KOH.....	74.9 cc.	75.9 cc.	24.6% CO ₂
Vol. after fuming H ₂ SO ₄	70.0 cc.	70.8 cc.	5.0% Hydrocarbons
Vol. after pyrogallol.....	69.4 cc.	70.2 cc.	0.6% O ₂
Vol. after cuprous ammonium.....	59.8 cc.	61.2 cc.	9.6% CO

10 cc. of the residue were then mixed with 50 cc. of air and exploded by means of an electric spark.

Vol. before explosion.....	60 cc.
Vol. after explosion.....	51.0 cc.
Vol. of contraction.....	9.0 cc.
Vol. after KOH.....	48.6 cc.
Vol. of CO ₂	2.4 cc.
Vol. of CH ₄ in 10 cc. residue.....	2.3 cc.
Contraction due to H ₂ + O ₂ in 10 cc. residue.....	4.6 cc.
Vol. of H ₂ in 10 cc. residue.....	3.1 cc.

Results for CH₄, H₂ and N₂ on basis of original gas:

Vol. of H ₂	18.8 per cent.
Vol. of CH ₄	13.0 per cent.
Vol. of N ₂	27.8 per cent. (by difference)

The density of the gas was found by Bunsen's diffusion method, as follows:

	Average time for series of experiments	Results
Air.....	26.85 seconds	1.000 sp. gr.
Sewage gas.....	22.99 seconds	0.733 sp. gr.
City gas.....	18.52 seconds	0.468 sp. gr.

In order to decompose the basic tarry distillate into more useful compounds, in the next series of experiments, the products of distillation were passed through a coil of $\frac{1}{2}$ inch gas pipe heated to bright redness. The coil was about 10 cm. in diameter and contained about 2.5 m. of pipe. It was expected that this would give a larger yield of gaseous products, and at the same time cause the decomposition of many of the complex organic bases into ammonia. Simultaneously the more valuable hydrocarbons of the benzol series ought to replace them in the tar. The only alteration, therefore, in the apparatus for this series of experiments, was the insertion of the superheating coil between the retort and the condenser. The procedure in the experiments remained the same as in the first series.

Under these conditions, the liquid distillate, which in the first series had the odor of pyridine and its homologues, now had the black color and characteristic odor of common coal tar. The amount, however, was less, the yield from 60 grams of sludge being on an average 8 grams. An aliquot part of the gas liquor was taken for the determination of ammonia, the gas being distilled off and titrated with standard acid. The yield was found to be on a basis of 0.27 kg. NH₃ per 100 kg. sludge.

The gas, as produced from the apparatus with the use of the superheater, was increased in quantity and improved in quality. A charge of 60 grams of sludge gave on an average 11.4-11.9 liters of gas, or on a basis of 19.08 cu. m. per 100 kg. sludge. When

burnt in a fishtail burner it gave a flame far brighter than the flame of the city gas. Analysis gave the following results, the procedure being the same as in the analysis of the gas made without the superheated which has been already described.

Vol. after KOH.....	81.2 cc.	82.0 cc.	18.4% CO ₂
Vol. after fuming H ₂ SO ₄	65.2 cc.	66.2 cc.	15.9% Hydrocarbons
Vol. after pyrogallol.....	64.5 cc.	65.4 cc.	0.7% O ₂
Vol. after cuprous ammonium.....	56.6 cc.	58.4 cc.	7.5% CO

10 cc. of the residue was then mixed with 40 cc. of air and exploded by means of an electric spark.

Vol. before explosion.....	50.0 cc.
Vol. after explosion.....	37.2 cc.	38.4 cc.
Vol. of contraction.....	12.8 cc.	11.6 cc.
Vol. after KOH.....	34.8 cc.	36.0 cc.
Vol. of CO ₂	2.4 cc.	2.4 cc.

Vol. of CH ₄ in 10 cc. of residue.....	2.4 cc.
Contraction due to H ₂ + O ₂	7.4 cc.
Vol. of H ₂ in 10 cc.....	4.9 cc.
Total vol. of CH ₄ in original gas.....	13.8 cc.
Total vol. of H ₂ in original gas.....	28.2 cc.
Total vol. N ₂ in original gas.....	15.5 cc. (by difference)

The density of the gas was found by Bunsen's diffusion method, as follows:

	Average time for series of experiments	Results
Air.....	22.20 seconds	1.000 sp. gr.
Gas.....	20.06 seconds	0.499 sp. gr.

SUMMARY

We can briefly recapitulate the results obtained in this work as follows:

1. That the sludge will become almost dry at ordinary temperatures in four days, or in less than ten hours if exposed to a mild, artificial heat.
2. That the yield of gas from the heated sludge is comparable to the yield from a ton of gas coal, if the products of distillation are passed through a superheater.
3. That the quantity of illuminating hydrocarbons in this gas is almost three times as great as in coal gas.
4. That the superheating of the tarry distillate changes its character from a substance resembling bone oil to what appears to be coal tar.
5. That the amount of ammonia is fully equal to that obtained from coal.

CHEMICAL LABORATORY, HARVARD COLLEGE
CAMBRIDGE, MASS.

ALLOYS OF COBALT WITH CHROMIUM AND OTHER METALS¹

By ELWOOD HAYNES

As in organic nature, certain animal and vegetable forms have undergone modifications, and thus, as it were, fitted themselves to live in a new environment, so it has been found possible in certain instances to form new metallic combinations which are practically immune to the natural conditions that exist on the earth at the present time. A few of the rare metals, such as gold, silver, and the metals of the platinum group, are found native, but the commoner heavy metals are nearly always found in the form of oxides or sulfides.

For a number of years I have made experiments with a view to finding certain metallic combinations

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

or alloys which would not only resist oxidation and other harmful influences, but would also possess valuable physical properties, which would render them fit for special services. The first decisive step made in this direction, was the discovery of an alloy of nickel and chromium in 1898. The properties of this alloy have already been described in a previous paper.¹ Immediately following the discovery of the nickel-chromium alloy, I produced an alloy of cobalt and chromium. This has likewise been described in the previous paper, but the range of proportion between the cobalt and chromium is so great, and the combination is modified to such a marked degree by the introduction of other substances, that I have felt justified in reading another paper on this subject, describing more fully my researches in this particular direction.

As early as 1907 and 1908, I made alloys or combinations of cobalt, chromium and tungsten; cobalt, chromium and molybdenum; and cobalt, chromium, tungsten and molybdenum. I have made alloys of cobalt and chromium containing zirconium, tantalum, thorium, titanium, vanadium, etc. I have also added to the cobalt-chromium alloys the non-metallic elements, carbon, silicon, and boron. Some exceedingly interesting results have been obtained from these various combinations, and while further investigation is necessary in order to fully determine their chemical and physical properties, a number of them have shown interesting economic possibilities.

The preliminary fusions were made in graphite crucibles by means of a furnace operated by natural gas. I was later obliged to use crucibles of a special composition, not only to avoid the contamination of the metal by carbon from the crucible, but also because they proved more reliable under long-continued heating, than those made of graphite.

The metal tungsten alloys readily with chromium and cobalt in all proportions. When added in small quantity to the cobalt-chromium alloy, it seems to have little influence on the properties of the combinations, but if the proportion rises to 2 per cent. or 3 per cent., a notable effect is produced. Generally speaking, the cobalt-chromium alloy becomes harder and more elastic, especially if it contains a small amount of carbon, boron, or silicon.

The following experiment shows the effect of melting the alloy in a graphite crucible: 90 grams of cobalt, 6.3 grams of tungsten, 18 grams of chromium, together with a small quantity of calcium silicide, were introduced into a graphite crucible. The resulting alloy was very hard, and the crucible much eroded on the inside. The bar could be slightly flattened at one end, and after being made into a cold chisel, showed remarkable qualities. It would not only scratch glass, but also quartz crystal. It was quite tough at ordinary temperatures, and would cut small chips or shavings from a piece of stellite. At a bright yellow heat it showed signs of fusion, and became covered with a skin of oxide.

An alloy was made by melting the following in a

special crucible: Cobalt rondelles 80 grams, chromium 20 grams, tungsten 7 grams, calcium silicide 10 grams, calcium carbide 5 grams. As soon as the above were melted, the crucible cover was removed, and 15 grams of an alloy of cobalt and boron were introduced. The crucible lid was then replaced and the heating continued. A heavy, thick slag formed, which was removed before pouring the metal. The resulting bar was very hard and *elastic*, but drew only slightly under the hammer, and then broke. A cold chisel made from the cast metal cut iron readily. The bar was broken up and remelted with about one-third of its weight of an alloy of cobalt, chromium, tungsten and carbon. The result was a fine-grained alloy which was very *elastic*, and would draw out to a considerable degree under the hammer without checking. Its elastic limit must have been very high, since when it broke, the pieces were thrown violently.

Taking the alloy of chromium and cobalt as a basis, and holding the proportion of chromium at 15 per cent. of the entire mixture, it was found that the alloy gradually increased in hardness with the percentage of tungsten. When the quantity of tungsten rises to 5 per cent., the alloy becomes distinctly harder, particularly when forged under the hammer. When the tungsten reaches 10 per cent., the metal still forges readily, and a tool formed from the alloy takes a fine cutting edge. This alloy is suitable for both cold chisels and wood-working tools. When the tungsten rises to 15 per cent., the metal can still be forged, but great care is necessary in order to avoid checking. This alloy is considerably harder than that containing 10 per cent. of tungsten and is excellent for cold chisels. When the tungsten rises to 20 per cent., the alloy is still harder, and can be forged to a small extent. It makes good lathe tools for cutting steel and other metals at moderate speeds. When the tungsten rises to 25 per cent., a very hard alloy results, which cannot be forged to any extent, but casts readily into bars which may be ground to a suitable form for lathe tools. These tools have shown great capabilities, particularly for the turning of steel, since they are very strong, and retain their hardness at speeds which almost instantly destroy the cutting edge of a steel tool. The tungsten may be still further increased to 40 per cent., and the alloy will retain its cutting qualities, and for turning cast iron, this alloy answers even better than that containing 25 per cent. When the tungsten reaches 40 per cent. or more, the alloy becomes so hard that it will not only scratch glass, but will readily scratch quartz crystal. A small drill, made of this material, drilled a hole through the wall of a glass bottle without the addition of any liquid or other lubricant. A three-eighth inch square cast bar, when ground to a suitable edge, was set in a tool holder attached to a lathe. The workman who had operated the lathe, had been able to turn to form 26 cast iron wheels in 10 hours with a steel tool of the same size. The stellite tool turned 49 of these wheels to form in the same time. The steel tool was ground 50 times during the operation, while the edge of the stellite tool was dressed slightly by a carborundum whetstone, after its day's work was

¹ THIS JOURNAL, 2, 397.

completed. A set of steel cutters, placed in the boring head of a cylinder-boring machine, were able to bore from 26 to 28 holes in 10 hours. These cutters were replaced by others made of stellite, which performed the work in 3 hours and 20 minutes, or a little more than one-third the time. Not only was the speed of the mill doubled, but the feed also, and notwithstanding this severe ordeal, the stellite cutters were only slightly worn, while it would have been necessary to regrind the steel cutters at least two or three times for the same service at slower speed. Some remarkable results were obtained in the turning of steel on the lathe. For example, a cylindrical bar of annealed nickel-chrome steel, about two and one-half inches in diameter, was placed in a lathe and turned with a steel tool at about as high a speed as the steel would permit without "burning." The steel tool was then replaced by one of stellite, and the speed at the same time increased to two and two-thirds its former speed. The stellite tool retained its edge under these severe conditions, and produced a shaving weighing one and two-tenths pounds in one-half minute. Just what the effect of the alloy will be in machine shop practice is at present somewhat difficult to determine. In my opinion, however, it will not fully supersede high-speed steel in the machine shop, but in cases where rapid work is the main consideration, it will doubtless replace high-speed steel.

When molybdenum is added to a 15 per cent. cobalt-chromium alloy, the alloy rapidly hardens as the molybdenum content increases, until the content of the latter metal reaches 40 per cent., when the alloy becomes exceedingly hard and brittle. It cuts keenly and deeply into glass, and scratches quartz crystal with ease. It takes a magnificent polish, which it retains under all conditions, and on account of its extreme hardness, its surface is not readily scratched. When 25 per cent. molybdenum is added to a 15 per cent. chromium alloy, a fine-grained metal results, which scratches glass rather readily, and takes a strong, keen edge. Its color and luster are magnificent, and it will doubtless find a wide application for fine, hard cutlery. It cannot be forged, but casts readily, and its melting point is not abnormally high.

If carbon, boron, or silicon be added to any of the above alloys, they are rendered much harder, though their effect is not always desirable, since they tend to render the alloys more brittle.

If either tungsten or molybdenum is added to a cobalt-chromium alloy containing 25 per cent. of the latter metal, the hardness of the alloy is rapidly increased. When the percentage of tungsten, for example, reaches 5 per cent., the alloy can be readily forged, and forms an excellent combination for wood-cutting tools, such as chisels, pocket knives, etc. When molybdenum is added to the same mixture of chromium and cobalt, much the same effect is produced, though, generally speaking, a smaller quantity of molybdenum is required to produce a given increase in hardness. In some instances I have found it advisable to add both molybdenum and tungsten to the cobalt-chromium alloys. Generally, the color and

luster of these alloys, after polishing, are magnificent, and they seem to resist atmospheric influences equally as well as the binary alloy of cobalt and chromium.

KOKOMO, INDIANA

THE RELATION OF THE PRODUCTION OF ALUMINA TO THE FIXATION OF NITROGEN¹

By SAMUEL A. TUCKER

The connection of nitrogen fixation and the production of alumina is to be found in the Serpek process and probably in this process only. The Serpek process is primarily one for the fixation of nitrogen, but necessarily involves the production of alumina as a by-product and this by-product is all important to the success of the process commercially.

Briefly the Serpek process takes alumina and carbon in the proportions to form aluminium nitride in a strongly heated atmosphere of nitrogen, or $\text{Al}_2\text{O}_3 + 3\text{C} + \text{N}_2 \longrightarrow 2\text{AlN} + 3\text{CO}$.

The range of temperature necessary for this reaction is from 1600°-2000° C. according to Serpek. The product obtained contains about 30 per cent. nitrogen in the form of aluminium nitride, and is thus considerably richer in fixed nitrogen than calcium cyanamid which rarely runs over 20 per cent.

This reaction appeared so important to me that I thought it was worth while to investigate it and in conjunction with Mr. H. L. Read, the process was tried on a small scale. The results of this work have been read at the recent Congress of Applied Chemistry,² and it will be unnecessary to repeat them here, excepting that we found that the reaction worked satisfactorily on a small scale, the product contained 30 per cent. of nitrogen, and that bauxite was the best material with which to supply the aluminium. The temperature is important; below 1600° C. practically no nitrogen is fixed; above 2000° C. decomposition is likely to occur. I would like to know more as to the influence of temperature, and I had expected to conduct some experiments on this point so that I might give you this information now, but an accident to the electric furnace prevented it.

The commercial product must be nearly pure aluminium nitride, and at first sight seems to consist of two forms, the blue and the yellow. Professor Luquer has examined these specimens microscopically, and while his examination has not yet been completed he tells me that the internal structure is the same; both are strong double refracting and show uni-axial structure. With our present information, it would be difficult to figure the cost of production of this material, and even the power necessary for its manufacture is probably not generally known.

The question of the necessary time to convert the charge is important and in our experiments we found that it had a great influence on the nitrogen content of the product. It therefore seems necessary that

¹ Presented at the Joint meeting of American Electrochemical Society, Society of Chemical Industry and American Chemical Society, Chemists' Club, New York City, February 7, 1913.

² See also *Met. Chem. Eng.*, 9, 745.

the mixture should be heated to a high temperature for a considerable time.

This is different from the Frank process for cyanamid, in that the temperature for the actual nitrogen fixation is relatively low. Granting that the process can be worked out on a satisfactory cost basis, we see that the production of alumina is an all-important consideration. By proper treatment of the Serpek product there seems to be no difficulty in obtaining the nitrogen as ammonia and the aluminum as alumina, and the latter should be practically pure Al_2O_3 .

It might be supposed that the alumina so produced could be used over again in the process, but aside from its value in connection with the aluminum industry, pure alumina is not advantageous as a raw material, as it requires a higher temperature than bauxite. The process is therefore necessarily associated with the production of aluminium. If we might suppose that the Serpek process were to be conducted on the same scale as the Frank process for cyanamid manufacture, it is evident that it would involve the production of a large amount of alumina. From figures recently published regarding the Frank process, we find that the capacity output of all the plants covering various parts of the world for 1912 is roughly 200,000 tons. If we figure this as containing 18 per cent. nitrogen, it involves the fixation of 36,000 tons of nitrogen. With the Serpek product at 30 per cent. nitrogen content, it would require the production of 120,000 tons to equal this, and after decomposing to obtain the ammonia as follows,



we obtain 149,200 tons of alumina. This quantity of alumina should give 79,104 tons of metallic aluminium.

In the year 1911 we find that the capacity of all the plants producing aluminium was 62,100 tons, but that the estimated production actually was about 45,000 tons. We thus have raw material for the production of 34,000 tons of alumina in excess of present requirements. Of course the process will not be conducted on such a scale for some time to come, and by that time there might well be a market for the alumina. There appears to be no danger from the lack of bauxite as I find that in this country 155,618 tons were produced in 1911, and 196,000 tons in France for the year 1910.

As the Serpek process would necessarily come into competition with the other means of fixing nitrogen, and particularly with the cyanamid process, it might be well to consider for a moment a few points in connection with the latter.

Briefly the Frank-Caro process for making cyanamid is to subject finely ground calcium carbide to the action of pure nitrogen at a temperature of from 1000–1200° C. The energy necessary at this absorption stage is probably very small, as heat is evolved by the reaction



and the expenditure of energy is chiefly in the manufacture of the calcium carbide. Various conditions

have to be observed in this absorption part of the process. The nitrogen must be practically free of oxygen and the temperature must not rise to the dissociation point of the cyanamid which is probably about 1370° C. The product so obtained contains anywhere from 15 to 22 per cent. of nitrogen. The nitrogen is obtained by passing air over copper to take up the oxygen, or by fractionally distilling liquid air. Both systems seem to be in use, but with the latter some treatment of the resulting nitrogen with copper would probably have to be employed as nitrogen obtained from liquid air contains upwards of 8 per cent. oxygen.

The process seems fairly complicated, but possesses the advantage over the high tension arc systems of fixation in that a better return of nitrogen is obtained for the power used. In the Frank process the chief expenditure for power is in the formation of calcium carbide. The average of several plants making carbide is 5.2 kg. of 80 per cent. carbide per kw. day of 24 hours. This gives 4.16 kg. of pure calcium carbide which corresponds to 173 grams per kw. hour. Now if this is converted to cyanamid having a 20 per cent. nitrogen content, we get 43.2 grams nitrogen per kw. hour.

The Birkeland-Eyde process obtains about 57.1 grams nitric acid per kw. hour and the nitrogen content is 12.7 grams. We thus have about three and one-half times the nitrogen fixed by the Frank process as cyanamid as we do for the Birkeland-Eyde process as nitric acid, and this is probably the reason for its being established on such a large scale.

As to the relative value of the fixed nitrogen fertilizers, we have no very precise information. Taking the various products adapted to this purpose in the different processes, we get calcium nitrate by the Birkeland-Eyde, calcium cyanamid by the Frank, and lastly ammonia by the Serpek process. These must all be compared with Chili sodium nitrate, and the general opinion seems to be that the latter is the most valuable.

Field experiments have been conducted with cyanamid and calcium nitrate, but precise information is lacking. It would seem, however, from what has so far been done, that we should put them in the following order:

(1) Chili saltpeter, (2) calcium nitrate, (3) cyanamid, (4) ammonia. The action of cyanamid is quite different from the others; it supplies a large amount of calcium which may or may not be an advantage. Its slow solubility is, however, advantageous. Ammonia in the form of sulfate is pretty well understood in its relation to fertilization and for that reason the Serpek product should have a ready market in this connection.

ELECTROCHEMICAL LABORATORY
COLUMBIA UNIVERSITY
NEW YORK

ON THE RELATIONSHIP BETWEEN THE WEIGHT OF THE SUGAR BEET AND THE COMPOSITION OF ITS JUICE

By J. ARTHUR HARRIS AND ROSS AIKEN GORTNER

Received October 14, 1912

In the voluminous literature of sugar beet chemistry published from the Federal and State agricultural

institutions, the weight of the beet, the per cent. of total solids and of sucrose in the juice, and the coefficient of purity, *i. e.*, the ratio of sucrose to 100 parts of total solids, are usually given.

Much of this work has been done for the purpose of ascertaining where sugar beets can be profitably grown. Roots below a certain standard of sucrose content and purity are, from well known factory requirements, unworkable. Records for size of beets have apparently been added because yield is assumed to be, in some degree, dependent upon size, and because size has been suspected to have some relation to composition.¹

This latter point has, however, been but little investigated, and we believe only by inadequate methods. It has seemed to us of importance to measure the intensity of this relationship on the -1 to $+1$ scale of the coefficient of correlation; also to write the regression equations showing the absolute change in solids, sugar, or purity, associated with a unit change in weight (in grams or ounces) of the beet. The importance of doing this seems to lie in three considerations:

(a) The working out of such inter-dependences is from the standpoint of physiology and phytochemistry, a problem of considerable interest.

(b) If the composition of the beet depends at all closely upon its size, the analysis of small samples sent in to government departments are practically worthless as indicating the practicability of localities for sugar beet growing. Even if the samples are not consciously selected for size, the errors of random sampling are such as to render practically valueless any conclusions drawn upon analyses which are not corrected for the size factor.

(c) Finally, if composition be closely correlated with size, it may be possible to modify the rate of seeding, methods of fertilization, or cultivation, in such a way as to secure the sugar yield which is most profitable in relation to the cost of growing and handling.

Suitable published data seem all but wanting. In many series the weights given are averages, without specification as to the number of beets included. Analyses have been made by the thousands, and in some cases upon uniform material drawn from the same cultural conditions, but we have not been able to obtain such records, either published or in manu-

script.² Hence, these notes serve merely to indicate the importance of the problem and the usefulness of the method of attack.

Table I gives the data slightly condensed from Wiley and Maxwell³ for sixty-one Washington Klein Wanzlebener beets. Tables II-V give mean compositions for various weights in ounces⁴ for four varieties from Nevada data.⁴ The calculations have also been made from the total Nevada material.

The correlation coefficients⁵ and the regression straight line equations are as follows, where w = weight,⁶ t = total solids, s = sucrose, p = purity:

KLEIN WANZLEBENER, WASHINGTON DATA⁷—TABLE I

$$\begin{aligned} r_{wt} &= -0.283 \pm 0.079, t = 15.459 - 0.012 w \\ r_{ts} &= -0.224 \pm 0.082, s = 10.903 - 0.011 w \\ r_{wp} &= -0.111 \pm 0.085, p = 70.176 - 0.018 w \end{aligned}$$

IMPROVED KLEIN WANZLEBENER, NEVADA DATA⁷—TABLE II

$$\begin{aligned} r_{wt} &= -0.538 \pm 0.060, t = 18.864 - 0.068 w \\ r_{ts} &= -0.756 \pm 0.036, s = 17.197 - 0.121 w \\ r_{wp} &= 0.499 \pm 0.063, p = 89.996 - 0.300 w \end{aligned}$$

VESBESSERTEN KLEIN WANZLEBENER, NEVADA DATA—TABLE III

$$\begin{aligned} r_{wt} &= -0.619 \pm 0.043, t = 20.040 - 0.092 w \\ r_{ts} &= -0.641 \pm 0.041, s = 16.819 - 0.106 w \\ r_{wp} &= -0.587 \pm 0.046, p = 85.956 - 0.276 w \end{aligned}$$

VILMORIN AMELIORÉE, NEVADA DATA—TABLE IV

$$\begin{aligned} r_{wt} &= -0.294 \pm 0.086, t = 19.266 - 0.090 w \\ r_{ts} &= -0.580 \pm 0.063, s = 18.054 - 0.223 w \\ r_{wp} &= -0.623 \pm 0.058, p = 95.038 - 0.905 w \end{aligned}$$

DESFAZ, NEVADA DATA—TABLE V

$$\begin{aligned} r_{wt} &= -0.512 \pm 0.058, t = 21.185 - 0.130 w \\ r_{ts} &= -0.472 \pm 0.061, s = 18.691 - 0.131 w \\ r_{wp} &= -0.173 \pm 0.076, p = 87.860 - 0.089 w \end{aligned}$$

ALL VARIETIES, NEVADA DATA, 475 BEETS

$$\begin{aligned} r_{wt} &= -0.497 \pm 0.023, t = 20.119 - 0.096 w \\ r_{ts} &= -0.576 \pm 0.021, s = 17.644 - 0.131 w \\ r_{wp} &= -0.474 \pm 0.024, p = 88.516 - 0.273 w \end{aligned}$$

Considering the shortness of the materials upon which they are based, these results are surprisingly consistent throughout. They show that composition and purity are very closely correlated with weight, and in such a way that as weight increases, total solids, sucrose and percentage purity fall rapidly. The rate of fall on the relative scale of -1 to $+1$ is shown by the coefficient of correlation, r , the rate in an absolute scale by the second term of the regression equation. We have prepared graphs of most of these

¹ We shall be grateful for the loan of any suitable series of data for more refined statistical analyses.

² H. W. Wiley and W. Maxwell, *Bull.* **39**, Bureau of Chem., U. S. Dept. Agr.

³ The weights are grouped in units of 5-oz. range. The numbers given are the centers, *i. e.*, 3 = 1-5, 8 = 6-10, etc.

⁴ N. E. Wilson, *Bull.* **32**, Nev. Agr. Exp. Sta.

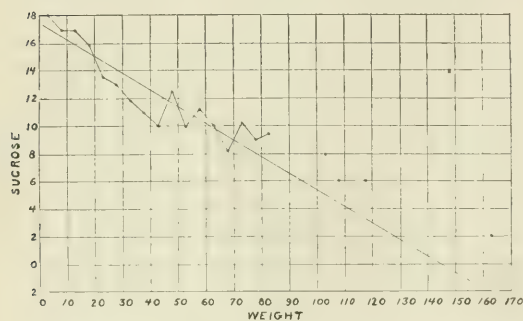
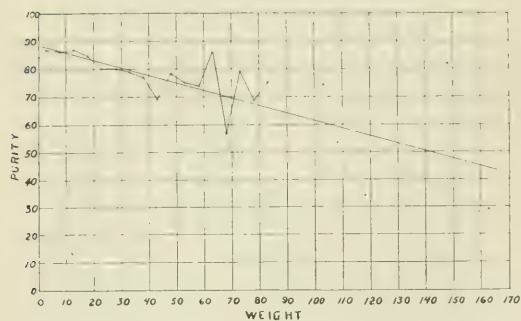
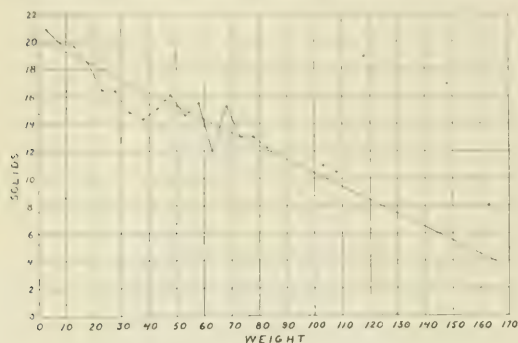
⁵ The methods of calculating the correlation coefficient and the regression equation can be found in various books on modern higher statistics. These for the first table have been worked out by the brute force method, summations, summations of squares, and summations of products being made directly. Those for Tables II-V have been made by the method described by Harris (*Amer. Nat.*, **44**, 693-699 (1910)) before the sums for each class weight were divided out to get the means, which show most clearly to the eye the changes in composition. Here again the means and standard deviations were obtained by the brute force method, the analyses being kept to one decimal place for solids and sucrose and to whole per cents. for purity.

⁶ In the Washington data the rate of change in per cent. total solids, per cent. sucrose, and per cent. purity, are calculated on weight units of 10 grams each. In the Nevada data the weight units are ounces.

⁷ *Loc. cit.*

¹ We have examined fifty-eight papers on the sugar beet, comprising bulletins from the Bureau of Chemistry, U. S. Dept. of Agr. and from twenty-two state experiment stations. In only five of these is the possible relationship between the weight of the beet and the sucrose content and purity coefficient considered. Two, *Bull.* **197**, Mich. Agr. Exp. Sta. and *Bull.* **68**, Purdue Univ. Exp. Sta., give experiments which indicate that the smaller the weight of the beet, the higher is the sugar content and coefficient of purity. Of the other three, *Bulls.* **58** and **63** of the Colorado Exp. Sta., state that "as a rule medium-sized beets (1-2 pounds) are richer than either large or small beets," and *Bull.* **155**, N. Y. Agr. Exp. Sta. (Geneva) contains the statement that "between these limits (5-27 oz.) the increase in size did not apparently exercise any marked or definite influence upon either the percentage or the purity of sugar." Doubtless other suggestions might be found, especially in foreign publications. It is perhaps generally admitted that excessively large beets (4 pounds and over) are as a rule low in sugar and have a low coefficient of purity, but, as far as we know, there has been no thorough investigation of the general problem of weight and composition.

equations and while the empirical means are very irregular there is no very clear evidence to show that regression is other than linear. The diagrams show



the lines and empirical means of the (heterogeneous) Nevada total material. Those means which are based upon a fairly satisfactory number of beets are joined up.

TABLE I—KLEIN WANZLEBENER

Key number	Weight in ten-gram units	Total solids	Sucrose in juice	Purity	Key number	Weight in ten-gram units	Total solids	Sucrose in juice	Purity
60	88	20.1	17.8	89	75	86	17.8	12.3	69
65	110	19.7	15.0	78	76	37	18.9	13.3	70
66	67	16.6	11.5	69	77	38	17.5	11.7	67
67	146	18.9	13.6	72	78	74	17.7	12.3	70
68	137	15.4	10.7	69	79	52	17.5	13.2	75
69	98	19.2	16.0	83	80	126	16.6	11.4	69
70	137	15.3	10.6	69	81	50	16.5	11.0	67
71	232	13.8	8.9	65	82	91	14.4	9.0	63
72	88	16.4	12.0	73	83	79	16.0	10.0	63
73	136	16.6	12.5	75	84	51	14.5	9.1	63

TABLE I—KLEIN WANZLEBENER (Continued)

Key number	Weight in ten-gram units	Total solids	Sucrose in juice	Purity	Key number	Weight in ten-gram units	Total solids	Sucrose in juice	Purity
85	164	14.8	9.8	66	138	109	13.6	9.4	69
86	120	15.0	10.0	67	139	86	14.0	9.8	70
97	102	17.0	11.9	70	140	140	13.7	8.5	62
98	88	16.8	11.8	70	141	54	14.1	8.0	57
107	98	17.9	14.3	80	142	74	15.1	11.0	73
108	88	16.0	11.5	72	143	84	15.0	11.3	75
110	61	17.1	11.6	68	144	92	16.5	11.6	70
111	50	15.9	11.2	70	145	74	16.3	11.5	71
112	48	15.2	9.7	64	146	55	13.5	9.6	71
113	33	17.0	11.8	69	147	82	15.2	11.9	78
114	54	17.9	13.2	74	148	109	15.5	10.7	69
116	33	17.7	11.0	62	149	54	16.7	12.4	74
117	38	18.5	13.9	75	150	72	16.4	11.4	70
118	91	16.9	13.6	81	151	65	15.8	10.6	67
120	85	17.7	14.5	82	152	47	17.0	13.4	79
121	72	16.5	12.8	78	153	37	19.3	13.3	69
123	40	16.5	12.6	76	154	50	18.8	15.4	82
130	157	16.2	12.0	74	155	58	14.3	10.3	72
131	65	17.5	13.7	78	156	95	17.5	13.1	75
135	45	16.5	14.8	90	157	127	15.7	11.2	71
137	126	15.2	10.0	66

TABLE II—IMPROVED KLEIN WANZLEBENER

Weight	N	Average solids	Average sucrose	Average purity
3	4	17.42	15.40	83.25
8	12	18.78	16.22	86.00
13	9	19.20	17.16	89.67
18	11	17.85	15.35	86.00
23	8	15.69	13.19	83.62
28	1	14.30	13.10	92.00
33	4	14.48	11.23	77.75
38	4	13.93	10.50	75.75
43	2	14.80	12.35	84.00
48	1	21.80	13.30	61.00
53	3	15.27	10.87	83.33
58	2	18.05	10.80	66.50
68	2	15.30	8.95	58.50
78	1	13.00	8.80	68.00
83	1	15.00	11.00	73.00

TABLE III—VERBESSETER KLEIN WANZLEBENER

Weights	N	Average solids	Average sucrose	Average purity
3	3	20.87	18.53	89.33
8	19	19.83	16.43	83.26
13	18	21.12	16.73	82.67
18	11	18.41	15.59	83.64
23	5	17.42	13.66	78.00
28	12	18.83	12.75	75.83
33	5	11.16	10.22	73.40
38	9	14.31	10.56	74.67
43	2	13.15	8.05	60.00
58	1	15.20	12.50	82.00
63	1	15.40	13.60	88.00
83	2	10.80	8.25	76.00
103	2	11.10	7.95	73.50
108	2	11.00	6.15	53.50
118	1	18.60	6.30	34.00
163	1	7.90	2.10	29.00

TABLE IV—VILMORIN AMELIORE

Weight	N	Average solids	Average sucrose	Average purity
3	2	19.60	17.00	86.50
8	3	17.60	12.56	90.00
13	6	19.57	17.13	87.16
18	13	17.70	13.97	79.08
23	11	16.65	11.60	70.25
28	8	16.06	11.38	70.37
33	6	17.73	12.11	68.50
43	1	14.40	8.00	54.00
53	1	15.60	7.00	45.00

TABLE V—DESPAREZ

Weight	N	Average solids	Average sucrose	Average purity
3	4	18.80	16.55	88.00
8	19	20.79	18.16	86.38
13	21	19.92	17.36	87.10
18	8	19.31	17.20	88.75
23	6	15.78	13.15	83.33
28	7	11.67	14.14	84.86
33	2	14.55	12.45	85.50
38	1	16.20	13.40	83.00
43	3	16.67	14.13	84.67
48	2	16.80	14.55	86.50
58	1	15.20	11.80	78.00

We believe that these results show with sufficient force the necessity of fully taking into account the weight of the individual beets in all studies on composition.

CARNEGIE INSTITUTION OF WASHINGTON

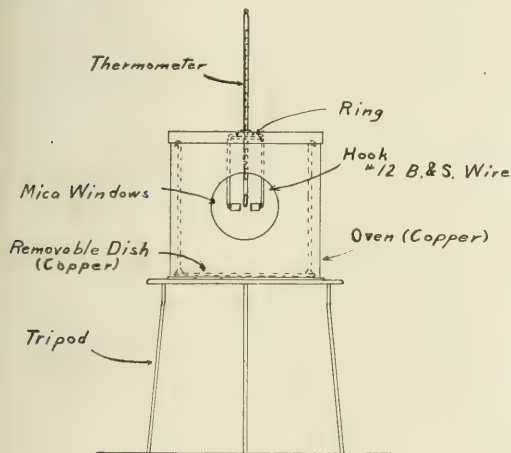
METHODS FOR TESTING COAL TAR, AND REFINED TAR, OILS AND PITCHES

By S. R. CHURCH

Received November 20, 1912

Under this title, the writer has given¹ a description of the methods used in our laboratories for testing the raw materials and products of tar distillation. It was intimated that certain of these tests would undoubtedly be revised from time to time, in response to suggestions from our own chemists as well as from others engaged in the examination of these materials.

It is our present purpose to describe the tests that have been revised since that paper appeared. It may be well also to call to the attention of those interested in testing tars, oils and pitches, a paper by



AIR BATH FOR MELTING POINT TEST.

Arthur R. Warnes and W. B. Southerton, before the Midland Junior Gas Association,² entitled "Investigations on Coal Tar and Some of Its Products," and to "Methods for the Examination of Bituminous Road Materials," by Prévost Hubbard and Charles S. Reeve.³

¹ THIS JOURNAL, 3, 227.

² Jour. Gas Lighting, etc., Feb. 27, 1912.

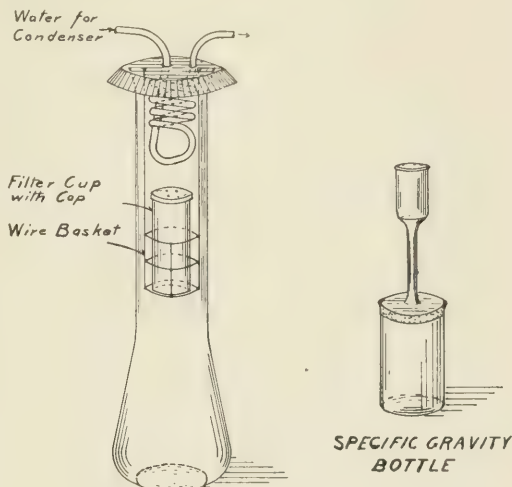
³ Bull. 38, Office of Public Roads, U. S. Department of Agriculture, July 27, 1911.

Owing to the comparatively recent appearance of our first paper on this subject, no reference will be made at present to the methods in which no change has been made.

TAR

B. Specific Gravity.—The special Hubbard type specific gravity bottle, referred to in the previous paper, was not illustrated. It is now shown on the accompanying drawing No. 2.

C. Free Carbon.—In place of the Knorr extraction



EXTRACTOR FOR FREE CARBON

apparatus, we have adopted the extractor illustrated in the accompanying drawing No. 2. This apparatus the writer first saw in use in the Underwriters' Laboratories, Chicago, and it has already been described.¹ In it we use the same filter papers as described in our former article. The filter cup is suspended from two hooks, soldered on to the upper side of the flask cover.

The advantages of this extractor over the Knorr or Soxhlet apparatus in making this determination are convenience, compactness, rapidity of operation.

E. Viscosity.—The time of flow of 100 cc. at 60° C. (140° F.) is taken, instead of 200 cc. as before. The quantity of material placed in the viscosimeter is the same, that is, sufficient to cover the fixed measuring points.

PITCH

C. Melting Point.—(3) For pitches from 77° C. (170° F.) upwards, an air bath, as shown in the accompanying drawing No. 3, is substituted for the bath of cottonseed oil formerly used. With this oven, shorter hooks are used, so that the pitch cube is suspended on a line running approximately through the center of the observation windows, the thermometer bulb being at the same level. The temperature of the oven is raised 5° C. (9° F.) each minute, as usual, and the temperature recorded by the thermometer at the instant the pitch drops to the bottom of the oven, is considered the melting point. To make

¹ H. J. Cary Curr, THIS JOURNAL, 4, No. 7

results by this method comparable with results obtained in water or oil, 6.5° C. (43.7° F.) should be added to the observed melting point.

E. Evaporation Test.—Reference was made to the use of a circular oven (of the type E. and A., 2073 D) having double walls, circulating fan and self-contained burner. Results obtained with this oven have not been entirely satisfactory, and an ordinary drying oven, lagged with asbestos, as before described, is still used for this determination.

CREOSOTE OIL—SPECIAL TESTS

C. Sulfonation Test.—The method before described, which was a modification of Dean and Bateman's method,¹ has been discarded in favor of a modification described by Bateman² as follows:

Apparatus.—Babcock's Official Milk Tester, with four bottles.

Description.—Ten cc. of the fraction of creosote to be tested are measured into a Babcock milk bottle. To this is added 40 cc. of 37 times normal acid, 10 cc. at a time. The bottle with its contents is shaken for two minutes after each addition of 10 cc. of acid. After all the acid has been added, the bottle is kept at a constant temperature of 98°–100° C. for one hour, during which time it is shaken vigorously every ten minutes. At the end of an hour the bottle is removed, cooled, and filled to the top of the graduation with ordinary sulfuric acid, and then whirled for five minutes in a Babcock separator. The unsulfonated residue is then read off from the graduations. The reading multiplied by two, gives per cent. by volume directly. (Each graduation equals one two-hundredths of a cc.)

It is important that the acid be of the proper strength. Fuming sulfuric acid is too strong, and ordinary concentrated acid too weak, a mixture of the two being required to obtain the necessary 80.07 per cent. SO₃, which constitutes 37 times normal.

A steam bath or steam-jacketed oven should be used for maintaining the bottle at a temperature of 98°–100° C.

RESEARCH DEPARTMENT
BARRETT MANUFACTURING CO.
NEW YORK CITY

THE COMPOSITION OF SALINES IN SILVER PEAK MARSH, NEVADA³

By R. B. DOLE, with analyses by WALTON VAN WINKLE AND A. R. MERZ
Received November 12, 1912

DESCRIPTION

Silver Peak Marsh, comprising the lowest part of Clayton Valley, lies in Esmeralda County, Nev., about 20 miles west of Goldfield and 25 miles southwest of Tonopah. It is about 10 miles long northeast and southwest and about 4 miles wide, its area being about 32 square miles. It is most readily reached by means of the Silver Peak Railroad, which connects with the Tonopah and Goldfield Railroad at Blair Junction and runs south to Blair, a small mining town near the western edge of the marsh. The marsh is a salt playa entirely devoid of vegetation and covered for the most part with a white crust of sodium chloride.

Tracts 3 or 4 acres in extent rising gently 1 to 3 feet above the general level appear as rough brown sun-baked patches without a covering of salt. The most noticeable topographic features are Goat and Alcatraz "islands," two groups of steep limestone hills near the southwest end of the playa. The surface of this alkali flat is usually dry, though it is sometimes covered by a foot or more of water after excessively heavy rainfall. The ground-water plane is, however, always high, and holes a few feet deep anywhere on the flat enter mud, many parts of the marsh being too soft to bear the weight of a horse. The present drainage basin of the valley has an area of 570 square miles.

EXPLORATION

In the spring of 1912 fourteen borings 8 to 55 feet deep were put down in different parts of the flat by the author for the purpose of exploring the surficial deposits. The upper layer, 5 to 10 feet thick, consists of brown mud containing a great quantity of finely crystallized salt. The strong brines in it circulate very slowly as the mud contains a large proportion of clay. The mud along the west shore bears nodules

TOTAL SALTS AND POTASSIUM IN BRINES FROM SILVER PEAK MARSH, NEV.,
JUNE, 1912

Examinations by A. R. Merz. Quantities in grams per 100 cc. unless otherwise designated

Boring No.	Depth of sample Feet	Total solids at 105° C.	Potassium expressed as			
			Potassium (K)	Potassium chloride (KCl)	Potassium oxide (K ₂ O) Percentage of potassium oxide (K ₂ O) in saline residue	
3.....	15.5	33.28	0.91	1.74	1.10	3.30
6.....	21	33.13	0.77	1.47	0.93	2.80
6.....	40	33.75	0.75	1.43	0.90	2.67
11.....	27	32.25	0.74	1.41	0.89	2.76
11.....	35	32.05	0.55	1.05	0.66	2.07
12.....	10	26.56	0.61	1.16	0.74	2.78
12.....	20	32.90	0.59	1.12	0.71	2.15
12.....	27	32.97	0.64	1.22	0.77	2.34
13.....	16	4.15	0.12	0.23	0.14	3.36
13.....	31.5	4.61	0.13	0.21	0.16	3.43
13.....	40	3.38	0.11	0.21	0.13	3.80
14.....	11	26.82	0.66	1.26	0.80	3.00
14.....	17	26.21	0.66	1.26	0.79	3.01

Average, exclusive of
samples from boring No.

13..... 30.99 0.69 1.31 0.83 2.69

of calcareous tufa, which apparently have been formed by deposition of calcium carbonate from the hard waters entering from Mineral Ridge. White tufaceous materials, but no definite beds of salt, underlie the muds in the same locality to a depth of at least 41 feet. Throughout the rest of the playa east of the "islands" the muds are underlain by salt clays intermingled with well-defined beds of clay containing crystals of gypsum and beds of crystallized salt containing saturated brine.

COMMERCIAL POSSIBILITIES

The records indicate that the northeastern two-thirds of the playa is underlain at a depth of about 20 feet by beds 5 to 15 feet thick of crystallized salt mixed with some clay. Besides these beds practically all other strata to a depth of 50 feet contain appreciable proportions of salt that readily dissolves in the waters percolating through them.

¹ U. S. Dept. Agric., Forest Service Circular 112.

² U. S. Dept. Agric., Forest Service Circular 191.

³ Published by permission of the Director, U. S. Geological Survey.

PARTIAL ANALYSES OF BRINES, SILVER PEAK MARSH, NEV.
Examinations by Walton Van Winkle. Milligrams per kilogram except where otherwise designated

Source	Depth Feet	Date, June, 1912	Specific gravity at 20° C.	Total residue		Carbonate radicle (CO ₃)	Bicarbonate radicle (HCO ₃)	Sulfate radicle (SO ₄)	Borate radicle (B ₄ O ₇)
				Dried at 180° C.	After ignition				
Boring No. 1.....	6	1	1.0281	39,330	38,620	0	532	570	..
	27	4	1.0406	57,600	56,240	Trace	327	582	..
Boring No. 3.....	15	5	1.2103	276,800	271,600	0	38	2,475	0
	21	7	1.2081	273,000	270,000	0	28	2,675	0
Boring No. 6.....	40	10	1.2082	274,000	270,000	0	36	2,395	0
	27	13	1.2105	274,000	271,700	0	74	4,955	0
Boring No. 11.....	35	14	1.2089	272,000	270,000	0	122	4,600	0
	10	15	1.1702	226,700	224,100	0	51	4,640	..
Boring No. 12.....	20	17	1.2097	274,500	270,900	0	45	4,030	..
	27	17	1.2098	274,700	271,300	0	50	3,900	..
	16	20	1.0284	39,950	38,860	0	803	476	..
Boring No. 13.....	31.5	21	1.0321	44,900	44,300	0	840	491	..
	40	22	1.0297	41,510	40,900	0	792	477	..
Boring No. 14.....	11	24	1.1747	233,200	228,800	0	39	2,250	..
	17	24	1.1697	227,900	223,500	0	33	2,090	..
Hot spring at bathhouse, Silver Peak.....	..	8	1.0217	30,670	29,960	0	533	..	Trace(?)
Cold spring at bathhouse, Silver Peak.....	..	8	1.0226	31,980	31,530	Trace	530	..	Trace
Cold spring at northeast end of marsh.....	..	14	1.0124	16,830	16,620	0	274	..	0
Hot spring at northeast end of marsh.....	..	14	1.0177	24,430	24,180	Trace	515
Spring at pumping station, Silver Peak.....	..	28	..	1,920	1,500	0	144
30-foot well at power house, Silver Peak.....	..	28	..	1,520	1,220	0	132

ANALYSES OF WATER FROM SILVER PEAK MARSH, NEV.
Walton Van Winkle, analyst

Composition in milligrams per kilogram												
No.	1	2	3	4	5	6	7	8	9	10	11	12
Specific gravity at 20° C.....	1.2089	1.2019	1.0300	1.1722	1.0217	1.0226	1.0124	1.0177	1.0406	1.0281
Silica (SiO ₂).....	0	20	50	0	80	20	30	40	40	40
Iron (Fe).....	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Aluminum (Al).....	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Calcium (Ca).....	1,800	940	790	2,800	580	420	130	220	470	490	170	150
Magnesium (Mg).....	650	290	1,030	100	70	70	20	40	270	190	58	56
Sodium (Na).....	97,180	95,190	13,620	77,480	9,650	10,110	5,770	8,370	19,210	13,030	352	195
Potassium (K).....	7,290	5,890	1,290	6,590	930	930	500	800	2,060	1,180	21	15
Carbonate radicle (CO ₃).....	0	0	Trace	0	0	Trace	0	Trace	Trace	0	0	0
Bicarbonate radicle (HCO ₃).....	40	70	700	40	533	530	270	520	330	530	144	132
Sulfate radicle (SO ₄).....	2,360	4,420	540	2,210	410	480	580	690	610	610	95	160
Chlorine (Cl).....	159,730	153,710	23,760	134,400	17,130	18,010	9,330	13,650	33,050	22,110	858(a)	548(b)
Total residue dried at 180° C.....	278,760	264,030	42,820	233,440	30,670	31,980	16,830	24,430	57,600	39,330	1,868	1,379
Total residue after ignition.....	270,990	262,670	41,610	228,440	29,960	31,530	16,620	24,180	56,240	38,620	1,672	1,209
Anhydrous residue (c).....	269,110	260,570	41,440	223,660	29,120	30,310	16,500	24,070	55,890	37,920	1,630	1,195
Percentage composition of anhydrous residues												
Silica (SiO ₂).....	0.00	0.01	0.12	0.00	0.28	0.07	0.18	0.17	0.07	0.11
Calcium (Ca).....	0.67	0.36	1.92	1.25	1.99	1.38	0.79	0.91	0.84	1.29	10.43	12.56
Magnesium (Mg).....	0.24	0.11	2.49	0.04	0.24	0.23	0.12	0.17	0.48	0.50	3.55	4.70
Sodium (Na).....	36.11	36.53	32.86	34.64	33.14	33.35	34.97	34.77	34.37	34.36	21.58	16.32
Potassium (K).....	2.71	2.26	3.12	2.95	3.19	3.07	3.03	3.33	3.69	3.11	1.28	1.26
Carbonate radicle (CO ₃).....	0.01	0.01	0.83	0.01	0.90	0.86	0.81	1.05	0.29	0.69	4.35	5.44
Sulfate radicle (SO ₄).....	0.88	1.70	1.30	0.99	1.41	1.58	3.52	2.87	1.09	1.61	5.83	13.40
Chlorine (Cl).....	59.35	58.99	57.33	60.09	58.82	59.43	56.55	56.70	59.14	58.30	52.62(a)	45.87(b)

(a) Nitrate radicle 5.6 mg. per kilogram, or 0.33 per cent.

(b) Nitrate radicle 5.0 mg. per kilogram, or 0.42 per cent.

(c) Computed on the assumption that iron, aluminum, borates, and other radicles constitute 0.03 per cent. of the anhydrous residue.

- Composite of samples from boring No. 3 at 15.5 feet and from No. 6 at 21 and 40 feet.
- Composite of samples from boring No. 11 at 27 and 35 feet and from No. 12 at 10, 20, and 27 feet.
- Composite of samples from boring No. 13 at 16, 31.5, and 40 feet.
- Composite of samples from boring No. 14 at 11 and 17 feet.
- Water from hot salt spring under bathhouse near Silver Peak, Nev., collected June 8, 1912.
- Water from cold salt spring at bathhouse near Silver Peak, Nev., collected June 8, 1912.
- Water from cold salt spring at northeast end of marsh, collected June 14, 1912.
- Water from hot salt spring at northeast end of marsh, collected June 14, 1912.
- Water from boring No. 1 at 6 feet, collected June 1, 1912.
- Water from boring No. 1 at 27 feet, collected June 4, 1912.
- Water from spring at pumping station, Silver Peak, Nev., collected June 28, 1912.
- Water from 30-foot well of Nevada-California Power Co. at Silver Peak, Nev., collected June 29, 1912.

Practically the entire surface of the playa, 32 square miles, is covered with salt that averages in depth about one-quarter of an inch. The upper muds, averaging probably 10 feet thick, contain not less than 2 per cent. of salt. It is estimated that not less than 15 square miles of the northeastern part contains a 10-foot saline bed of which at least 60 per cent. is salt. It is calculated from these moderate estimates that 15,000,000 tons of salt lie within 40 feet of the surface. The high rate of evaporation, which would permit solar concentration of brines, the absence of long-continued rainfall to interfere with operations, the nearness of a railroad, and the high degree of purity of the product as indicated by analyses of the brines are extremely favorable features in considering the possibility of

utilizing these deposits. Salt is now being produced on a small scale. Brines from pits in the upper muds or from furrows filled with rain water that has become saturated are concentrated and crystallized by solar evaporation in shallow vats dug in the playa, and the salt thus obtained is bagged for sale.

COMPOSITION OF THE BRINES

Samples of the brines were tested for potash by A. R. Merz at the Coöperative Laboratory, Mackay School of Mines, Reno, Nev. Partial analyses of the brines and more nearly complete analyses of composite samples of the brines also were made by Walton Van Winkle in the Coöperative Laboratory of the United States Geological Survey at Willamette University, Salem, Oregon.

The analyses show that the brines from the main salt body are essentially solutions of sodium chloride remarkably uniform in composition and concentration. Analyses Nos. 1, 2, and 4, of waters from borings Nos. 3, 6, 11, 12, and 14, indicate that the brines contain less than 2 per cent. of sulfate and 0.02 per cent. of carbonate. Only traces of borate were found. These brines on evaporation would yield a mass containing about 90 per cent. of sodium chloride and the character of the other ingredients makes it certain that a much purer product could be obtained by one crystallization. The differences in the amounts and proportions of the alkaline earths are especially noteworthy, as they indicate progressive steps in the concentration and deposition of those substances.

The content of potassium is too low to be of commercial importance. The anhydrous residues of the brines represented by analyses Nos. 1, 2, and 4 average 2.64 per cent. in content of potassium (K). The average potassium content of the same brines according to Merz is 2.23 per cent. of the saline residue dried at 105° C. This apparent discrepancy in estimates is, however, caused mostly by difference in unit of expression, the actual determinations of the radicle being equivalent respectively to 0.79 and 0.69 gram of potassium (K) per 100 cc. of brine.

SUMMARY

Silver Peak Marsh is a salt playa containing a high grade of sodium chloride. No extensive deposits of potash-bearing salts were found. To a depth of 50 feet the formations are chiefly salt clays and muds with layers of crystallized salt covered irregularly by gypsum-bearing clays. It is estimated that 15,000,000 tons of salt lie within 40 feet of the surface of the playa.

UNITED STATES GEOLOGICAL SURVEY
WASHINGTON, D. C.

COMPOSITION OF THE WATER OF CRATER LAKE, OREGON¹

By WALTON VAN WINKLE AND N. M. FINKBINER

Received November 14, 1912

Crater Lake, in the heart of the Cascade Mountains of Oregon, is one of the most interesting spots in the United States, both to scientist and to tourist. Popular accounts of its beauties have been published in magazines and its chief features of scientific interest

have been admirably set forth.² But though analyses of typical rocks are given in Diller and Patton's paper, no analysis of the water of the lake has yet appeared in print, and the subjoined analysis may, therefore, be useful to those interested in this remarkable body of water.

The following brief description of the lake, based on Diller's report and on personal observations by the senior author, makes the analyses more readily understandable. Crater Lake is situated in a geologically recent caldera occupying the site of a once lofty volcanic peak—Mount Mazama—in the midst of the Cascade Range, about 55 miles northeast of Medford, Oregon. The rim of the caldera is from 7,000 to 8,000 feet above the sea, and the lake surface was 6,175 feet, above sea level in 1908. The inner slope of the rim bears, in some places, a sparse growth of pine, but in many

ANALYSES OF WATER OF CRATER LAKE AND WOOD AND ROGUE RIVERS, OREGON

	Milligrams per liter			Percentage of anhydrous residue		
	Crater Lake ¹	Wood River ²	Rogue River ³	Crater Lake	Wood River	Rogue River
Total dissolved solids (heated to 180° C.)	80	81	71
SiO ₂	18	37	26	22.36	49.82	38.86
Fe	0.02	0.20	0.01	0.02	0.27	0.02
Ca	7.1	5.7	5.7	8.82	7.68	8.51
Mg	2.8	2.0	2.6	3.48	2.69	3.89
Na	11	7.2	7.2	{ 13.67 }	{ 9.69 }	{ 10.76 }
K	2.2					
CO ₃	0.0	0.0	0.0	21.11	18.85	29.89
HCO ₃	34	28	40	a	a	a
SO ₄	11	7.6	3.8	13.67	10.23	5.68
Cl	11	0.6	1.5	13.66	0.67	2.24
NO ₃	0.38	0.06	0.10	0.47	0.10	0.15
PO ₄	0.01	b	b	0.01

¹ Collected August 27, 1912, by M. Mecklem about 1 mile from shore at depth of 6 ft. Analysis by N. M. Finkbinder.

² Collected August 26, 1912, by Walton Van Winkle at bridge near Fort Klamath, Oregon. Analysis by Walton Van Winkle and N. M. Finkbinder.

³ Composite of daily samples Aug. 6-15, 1912, inc., collected at power house, near Tolo, Ore. Analysis by Walton Van Winkle and N. M. Finkbinder.

a HCO₃ computed to CO₃.

b Not determined.

others its walls drop sheer to the water's edge, here and there fringed by steep talus slopes. The surficial area of the lake is approximately 21 square miles, and its drainage basin is only about 6 square miles larger. The greatest depth of water is 1,996 feet, and a cinder cone projects more than 760 feet above the surface at the western extremity of the lake to form Wizard Island. Precipitation is more than 70 inches a year, occurring chiefly as snow in winter. Evaporation is less than 55 inches, and this, with loss by percolation, almost completely balances the inflow, there being no surface outlet to the lake. Some of the water may find its way by percolation into Rogue River, but more of it probably goes southeastward appearing as springs in the drainage basin of Klamath Lake.

As loss by percolation is only about one-third of the loss by evaporation, analyses of the water of the lake may be expected to give chemical evidence of slow

¹ J. S. Diller and H. B. Patton, "The Geology and Petrography of Crater Lake National Park," *Prof. Paper U. S. Geol. Survey*, 3 (1902); J. S. Diller, "Geological History of Crater Lake," *Department of the Interior*, 1912.

¹ Published by permission of the Director, U. S. Geological Survey.

concentration. That the analysis really shows concentration almost identical with that of other surface waters of the region is explained, however, by the fact that no sedimentary materials are exposed, the andesites, dacites, and basalts forming the basin of the lake, being nearly insoluble in the cold water, and, therefore, incapable of rapidly increasing its content of mineral matter. Concentration of chlorides is great as compared with that of other materials, an indication of the concentrated character of the water. As the published analyses of rocks indicate that almost no chloride exists in these formations, it is possible that the high percentage of that radicle in the water is due almost entirely to accumulated "cyclic" chlorine precipitated with the rain and snow. The unexpectedly high percentage of sulfates is possibly caused by solution of sulfur that remained in the bottom of the caldera in a more or less oxidized condition at the cessation of active volcanism. No other features of the analysis seem unusual, when it is compared with the accompanying analysis of waters collected from Wood and Rogue rivers in the same season.

U. S. GEOLOGICAL SURVEY
SALEM, OREGON

ACTION OF FERMENTING MANURE ON REINFORCING PHOSPHATES¹

By W. E. TOTTINGHAM and C. HOFFMAN
Received October 21, 1912

INTRODUCTION

For many years phosphorus² has held a position of importance in the established practice of applying fertilizers to the soil. Indeed, this particular element may be the limiting factor of fertility in some normal types of soil³ or it may become such by depletion in excessively cropped soils.⁴

The chief raw materials supplying phosphorus for the fertilizer trade are bones and rock-phosphate. In finely divided condition these materials are known as bone meal and ground rock-phosphate or floats, respectively. They appear to consist essentially of basic phosphates of calcium and supply phosphorus in forms comparatively insoluble in water and in weak saline solutions.

The fertilizer industry furnishes more soluble forms of phosphorus derived from the crude phosphates by treating them with strong sulfuric acid. These products are monocalcium phosphate, soluble in water, and di-calcium phosphate, slowly acted upon by water and attacked by warm, neutral solution of ammonium citrate, which dissolves a considerable part of the phosphorus. Commercial acid phosphate is a mixture of these products with calcium sulfate, also formed in the reaction. The term "available phosphoric acid" as used in the fertilizer trade designates the combined amounts of phosphorus (expressed as P_2O_5) obtained in water extract and citrate extract successively from

the same sample. It may include other forms than the mono- and dicalcium phosphates.

The increased cost of phosphorus in acid-phosphate as compared with the crude materials has been rather generally supposed to be justified by superior availability to plants, consequent upon its greater solubility. It is true that acid-phosphate has generally given results in the year of application superior to those from rock-phosphate. Yet it is generally recognized that the phosphorus supplied in this form is rapidly fixed in insoluble form by reaction with calcium carbonate and other soil minerals⁵ or reverted in the dilute soil solution to more basic and less soluble phosphates of calcium.⁶ The efficiency of acid phosphate is to be attributed, therefore, probably to the facility with which it permits phosphorus to be distributed through the soil in finely divided form, rather than to a permanent state of solubility. This important effect of fineness and thorough distribution in promoting availability has been recognized with reference to rock-phosphate and experiment stations have advised the farmer to purchase it under guarantee of fineness as well as of phosphorus content.

Considerable evidence has accumulated³ which indicates advantage from the use of finely ground rock-phosphate directly as a fertilizer, especially when it is applied in conjunction with a liberal supply of organic matter turned into the soil. Thorne⁴ and others have demonstrated considerable efficiency of rock-phosphate when applied to the soil as a mixture with farm manure, and this method of application for both rock-phosphate and acid-phosphate has been widely adopted in practice. The effect of decomposing organic matter upon rock-phosphate under these conditions, as observed in increased yield of crop, has been commonly attributed to organic acids. It has been stated that such acids produced in the fermentation of the organic matter liberate soluble phosphorus from the floats. Favorable results from this treatment have been observed to be generally most pronounced in seasons succeeding the year of application.

Experiments in which solvents commonly used for this purpose have been employed to determine any increase of available phosphorus in fermented mixtures of crude phosphates and organic matter have given, however, negative results. Fleischer⁵ analyzed water extracts from fermented mixtures of moss turf and ground phosphorite in varying proportions and found no appreciable increase of soluble phosphorus during periods of $4\frac{1}{2}$ to 9 months. In many cases the results showed decreases of water-soluble phosphorus. Pfeiffer and Thurman⁶ found that a crude phosphate

¹ See Farsky, *Abstr. in Bied. Centrbl.*, 1883, S. 449, and Schreiner and Failyer, *Bur. Soils, U. S. Dept. Agr., Bull.* 32.

² See Cameron and Bell, *Bur. of Soils, U. S. Dept. Agr., Bull.* 41, pp. 21 and 35; also Cameron and Seidell, *J. Am. Chem. Soc.*, 26, 1461.

³ Some of the most extensive data have been obtained by Merrill (Maine Expt. Sta., *Rpt.* 1898, p. 64), Hess (Penn. Expt. Sta., *Rpt.* 1895, p. 157), Goessmann (Hatch Expt. Sta., *Rpt.* 1897, p. 190), Jordan (Maine Expt. Sta., *Rpt.* 1894, p. 23), Wheeler, R. 1 Expt. Sta., *Bull.* 118 and Patterson (Md. Expt. Sta., *Bull.* 114).

⁴ Ohio Expt. Sta., *Bull.* 183, p. 206; *Circ.* 104, p. 15.

⁵ *Lands. Jahrb.*, Bd. 12, S. 186.

⁶ *Lands. Vers. Stat.*, Bd. 47, S. 353.

¹ Published with the permission of the Director of the Wisconsin Experiment Station.

² In the fertilizer industry and in agricultural practice phosphorus is commonly dealt with in terms of phosphoric acid anhydride, P_2O_5 . The term "phosphoric acid" used in this paper signifies P_2O_5 .

³ Hopkins and Pettit, *Ill. Expt. Sta., Bull.* 123, p. 239.

⁴ Whitson and Stoddart, *Wis. Expt. Sta., Research Bull.* 2, p. 45.

after contact for three months with a fermenting mixture of peat meal and liquid manure yielded only a trace of water-soluble and a slight increase of citrate-soluble phosphorus. Lupton¹ fermented cotton-seed and cotton-seed-meal separately with ground South Carolina phosphate rock. Frequent analyses, during a period of three months, gave variable results and indicated little, if any, increase in the availability of phosphorus. McDowell² analyzed a mixture of cow and horse manure and crude Tennessee rock-phosphate which had fermented slightly over a year but found no increase of either water-soluble or citrate-soluble phosphorus as a result of fermentation. Egorov,³ on the other hand, observed large decreases in the solubility of the phosphorus in fermenting mixtures of manure and rock-phosphate.

EXPERIMENTS WITH ROCK-PHOSPHATE AND MANURE

The work to be described in this paper included studies of the action of fermenting manure on rock-phosphate or floats conducted essentially after the method of McDowell.⁴ The fresh manure free from litter, which was a mixture of one-third horse manure and two-thirds cow manure unless specified otherwise, was thoroughly hand-mixed with floats in the proportion of one pound of floats to fifty pounds of manure.⁵ The samples were fermented in covered iron pails; and water was added occasionally in the earlier experiments to maintain a fairly even moisture content of the check and reinforced manures. Determinations were made as follows:

Moisture.—One hundred grams of fresh sample were dried to constant weight in a steam oven at 100° C.

Water-soluble Phosphoric Acid.—One hundred grams of fresh sample were extracted for five hours in a shaking machine at room temperature. The extract was then filtered and washed as rapidly as possible on a thick layer of paper pulp in a Büchner funnel, using ten successive 75 cc. portions of distilled water for the washings. Extract and washings were made to 2 liters and phosphoric acid determined in 200 cc. aliquots by the Neumann method.⁶

Citrate-soluble Phosphoric Acid.—The residue from the water extraction together with the filter pulp, sucked as free from water as possible, was transferred to a 1 liter Erlenmeyer flask with 800 cc. of neutral ammonium citrate solution⁷ at 65° C. Extraction with this solvent was continued for one-half hour at 65° C., shaking at five-minute intervals. The extract was filtered as before and washed to a volume of 1500 cc. with water at 65° C. The solution was then made to 2 liters and phosphoric acid determined in 100 cc. aliquots by Neumann's method. The citrate-soluble added to the water-soluble gives the available phosphoric acid.

N/5 Nitric-Acid-soluble Phosphoric Acid.—The resi-

due (with filter) from the citrate extraction was extracted for five hours with N/5 HNO₃ at room temperature (about 27° C. in all cases) in a shaking machine. The extract was filtered on paper pulp in the manner already described,⁸ washed with cold water to a volume of 1750 cc., and made to 2 liters. Aliquots of 200 cc. were analyzed for P₂O₅ by the Neumann method.

Total Phosphoric Acid.—Phosphoric acid was determined on the ground and mixed residue from the moisture determination, using the Neumann method.

In a preliminary experiment in which only cow manure was used the check manure showed a loss of 34.7 per cent. of the water-soluble phosphorus originally present and no loss of available phosphorus after 61 days of fermentation. In the floats-manure mixture the water-soluble phosphorus decreased by 65.4 per cent. of the original and the available phosphorus decreased by 39.6 per cent. of that originally available. After 96 days the check manure had lost 25.5 per cent. of the originally water-soluble phosphorus and 5.4 per cent. of the phosphorus originally available. During this time the mixture lost 63.6 per cent. of the water-soluble phosphorus and 25.8 per cent. of the available phosphorus, based on the respective original amounts of these constituents. There was, therefore, some recovery of water-soluble phosphorus in the check and of available phosphorus in the mixture during the later stages of fermentation. The losses of phosphorus appeared to warrant further investigation.

On August 17, 1909, a mixture of cow and horse manures was prepared and two 25-pound portions were fermented in the manner already described, one portion serving as a check and the other being mixed with one-half pound of rock-phosphate. A temperature of about 25° C. was maintained throughout the experiment. Liberation of ammonia was little evident after October 11th and by January 5th fermentation was progressing slowly. On the latter date sufficient water was added to the mixture to give it a percentage of moisture approximately equal to that of the check. Extractions and analyses were made by the methods already described and with the results given in Table I. By weighing the pails at samplings data were secured for calculating the losses of dry matter, due account being taken of rock-phosphate removed in sampling. In the columns succeeding the data for water-soluble, available and total-soluble phosphoric acid are given their respective values in percentages of the total P₂O₅.

The data of Table I show that the water-soluble phosphorus decreased during fermentation. In the check manure the loss for the 92-day period amounted to 32.0 per cent. of the total and 36.9 per cent. of that originally soluble. The mixture suffered corresponding losses of 15.1 per cent. and 44.0 per cent., respectively. Citrate-soluble phosphorus increased in the check manure and remained practically constant in the mixture. Consequent decrease of available phosphorus in the check sample was 19.4 per cent. of the total and of the originally available phosphorus. The available phosphorus of the mixture decreased

¹ Ala. Expt. Sta., *Bull.* 48.

² Penn. Expt. Sta., *Rpt.* 1907-1908, p. 177.

³ Abstr. in *Expt. Sta. Record*, 26, 2, 123.

⁴ *Loc. cit.*

⁵ The floats were furnished by the Michigan Carbon Works of Detroit and contained 27.58 per cent. total and 1.2 per cent. available P₂O₅.

⁶ Throughout this investigation phosphorus was finally weighed as Mg₂P₂O₇ according to the standard gravimetric method.

⁷ *Bur. Chem., U. S. Dept. Agr., Bull.* 107 (revised), p. 1.

by 13.7 per cent. of the total phosphorus and 25.9 per cent. of the phosphorus originally available. The losses in the respective samples and the proportional losses of check and mixture show general agreement with the results of the nearly equal period covered by the preliminary experiment. Added extraction with *N/5* nitric acid recovered all but 14.0 per cent. of the total phosphorus in both samples after 92 days of fermentation. This extracting agent, which has been used for determining tricalcium phosphate in soils,¹ was used in the hope to detect marked changes of phosphorus other than simple reversion to tricalcium phosphate.

For the entire period of fermentation covering 190 days, the check sample lost water-soluble phosphorus equal to 21.1 per cent. of the total and 24.34 per cent. of that originally soluble. This was a recovery of solubility over that observed at 92 days and conforms with the results of the previous experiment. With the mixture there was a loss of 19.6 per cent. of the total or 57.14 per cent. of the originally water-soluble phosphorus. The available phosphorus in the check at the close of the experiment was less than at the beginning by an amount equal to 13.4 per cent. of the total and of the available phosphorus

carbonate. Having found the ammonia content of a rapidly fermenting sample of horse manure equivalent to a 0.07 per cent. solution of ammonium carbonate in the moisture of the fresh manure, extractions were made with this solvent at the two later extractions of the last experiment. Separate 100 gram portions of the sample were treated with 1 liter portions of the solvent, the work being carried out as already described for water extracts. On November 19th the water extract of the check sample contained 54.7 per cent. of the total phosphorus, while the ammonium carbonate extracted 59.4 per cent. of the total. These solvents extracted 19.2 per cent. and 20.1 per cent., respectively of the total phosphorus in the mixture. On February 25th, water and ammonium carbonate extracted 65.6 per cent. and 45.7 per cent., respectively of the total phosphorus in the check. In the case of the mixture, these solvents extracted 14.7 per cent. and 10.4 per cent., respectively, of the total phosphorus. The results do not indicate that ammonium carbonate, as a product of fermentation, is an especially effective factor in rendering phosphorus available in fermenting manure.

Carbon dioxide formed by the decay of crop residues and dissolved in the soil water has been recognized

TABLE I.—PERCENTAGES OF PHOSPHORIC ACID IN THE DRY MATTER OF CHECK MANURE AND MANURE-FLOATS MIXTURE

Sample and date of analysis	Period of fermentation, days	Dry matter in manures, Per cent.	Loss of dry matter, Per cent.	Total P_2O_5 , Per cent.	Water-soluble P_2O_5		Citrate-soluble P_2O_5 , Per cent.	Available P_2O_5		$N/5$ nitric acid-soluble P_2O_5 , Per cent.	Total soluble P_2O_5	
					Per cent. of manure	Per cent. of total P_2O_5		Per cent. of manure	Per cent. of total P_2O_5			
Check												
Aug. 19.....	...	22.18	...	1.80	1.56	86.7	0.29	1.85	102.8	0.02	1.87	103.9
Nov. 19.....	92	17.60	31.20	2.54	1.39	54.7	0.73	2.12	83.4	0.08	2.20	86.6
Feb. 25.....	190	17.07	50.32	2.99	1.96	65.6	0.71	2.67	89.4	0.13	2.80	93.7
Mixture												
Aug. 19.....	...	23.65	...	4.70	1.61	34.3	0.87	2.48	52.8	1.78	4.26	90.7
Nov. 19.....	92	20.81	31.14	6.40	1.23	19.2	1.27	2.50	39.1	3.00	5.50	86.0
Feb. 25.....	190	21.30	50.97	7.67	1.13	14.7	0.95	2.08	27.1	3.67	5.75	74.7

originally present. In the mixture the corresponding losses were 25.7 per cent. of the total and 48.7 per cent. of the available phosphorus.

The data agree with those of the previous experiment, indicating pronounced suppression of water-soluble and of available phosphorus as measured by the standard reagents used for estimating these constituents of manures. At the close of the experiment additional extraction with *N/5* nitric acid recovered all but 6.3 per cent. and 25.3 of the total phosphorus in check and mixture, respectively. In the latter sample, at least, it appears that some change other than simple reversion to tricalcium phosphate occurred. Possible formation of organic compounds, especially of nuclein compounds by the action of bacteria, appears worthy of consideration as an explanation of the change.

Having found the phosphorus of fermented manure-floats mixtures depressed in availability as measured by solvents in common use it appeared that the natural solvent formed by the moisture of the fermenting manure might be a more efficient extractive agent. This solvent must contain considerable dissolved material, chief among which would be presumably ammonium

as an efficient solvent for soil phosphates since the time of Liebig. Many laboratory tests made to determine its solvent power for various phosphates also have demonstrated its efficiency. In the present investigation a solution of CO_2 saturated at room temperature proved about five times as efficient as water, or 0.07 per cent. ammonium carbonate solution in dissolving phosphorus from the rock phosphate. This extracting agent was applied also to the samples represented in Table I, after they had fermented 318 days. The results are given in Table II.

TABLE II.—PERCENTAGES OF PHOSPHORIC ACID IN DRY MATTER OF MANURE AND MANURE-FLOATS MIXTURE AFTER 318 DAYS OF FERMENTATION

Manure sample	Dry matter of manure, Per cent.	Total P_2O_5 , Per cent.	Water-soluble P_2O_5		P_2O_5 soluble in sat. solution of CO_2	
			Per cent. of manure		Per cent. of total	
			Per cent.	Per cent. of total P_2O_5	Per cent.	Per cent. of total P_2O_5
Check.....	42.70	3.08	0.60	19.48	0.87	28.25
Mixture.....	81.85	6.53	0.22	3.37	0.33	5.05

The data differ notably from those for the extraction after 190 days of fermentation (Table I, date of February 25th), since water recovered less than one-third of the phosphorus soluble in the check

¹ Stoddard, Wis. Expt. Sta., *Research Bull.* 2, 59.

manure and only about one-fourth of that soluble in the mixture at the earlier date.

This seems to indicate a marked conversion of phosphorus to forms less soluble in water, the effect being especially marked where floats were present. Carbon dioxide was decidedly superior to water for it recovered about 50 per cent. more phosphorus from both samples than did the latter solvent. The results of this extraction are not comparable with those already reported for ammonium carbonate because of the great difference in condition of the manures. They present evidence of greatly depressed solubility of phosphorus in water at an extreme stage of fermentation. The superiority of the carbon dioxide solutions appears to indicate that some of the phosphorus previously involved in the process of fermentation and rendered insoluble in water, had been liberated finally as inorganic phosphates insoluble in water but soluble in carbon dioxide solution. The results would seem to indicate, therefore, that carbon dioxide may be the chief agent involved in finally placing insoluble phosphorus of manures at the disposal of growing crops.

The work already presented suggested two points

TABLE III.—PERCENTAGES OF PHOSPHORIC ACID IN THE DRY MATTER OF NORMAL AND TREATED MANURE-FLOATS MIXTURES

Sample and date of analysis	Period of fermentation, days	Dry matter in manure, Per cent.	Loss of dry matter, Per cent.	Bacteriological count on gelatin, media, millions per gram dry manure	Total P ₂ O ₅ , Per cent.	Water-soluble P ₂ O ₅		Citrate-soluble P ₂ O ₅ , Per cent.	Available P ₂ O ₅		N/5 nitric acid-soluble P ₂ O ₅ , Per cent.	Total-soluble P ₂ O ₅		H ₂ CO ₃ soluble P ₂ O ₅	
						Per cent. in manure	Per cent. of total		Per cent. in manure	Per cent. of total		Per cent. in manure	Per cent. of total		
1. Normal															
Apr. 17	25	21.57		2190	4.21	1.40	33.26	0.63	2.03	48.21				1.26	29.89
May 12	25	19.12	14.90	218	4.71	0.98	20.81	0.88	1.86	39.55				1.40	29.77
July 6	80	16.95	38.81	4	5.69	1.00	17.57	1.11	2.11	37.08	3.27	5.38	94.62	1.08	18.98
2. With chloroform															
Apr. 17		21.72		344	4.21	1.37	32.54	a						1.25	29.66
May 12	25	22.05		1	3.91	1.32	33.76							1.47	37.57
July 6	80	21.82	1.13	0.1	4.13	1.16	28.11	0.48	1.64	39.73	2.15	3.79	91.77	1.05	25.42
3. With formalin															
Apr. 17		21.70		0	4.21	1.24	29.45	0.69	1.93	45.84				1.05	24.94
May 12	25	21.72		0.1	3.90	1.23	31.54	0.47	1.70	43.59				1.46	37.44
July 6	80	20.57	1.61	0	3.91	1.05	26.85	0.70	1.75	44.75	2.18	3.93	100.40	0.88	22.51

a Citrate extracts from chloroformed sample were lost at first and second extractions.

upon which it would be important, to direct further investigation:

First, the cause of the decrease of water-soluble phosphorus which was observed with manures and manure-floats mixtures.

Second, the efficiency of carbonated water as a solvent for phosphorus of actively fermenting manure.

Behrens¹ states that microorganisms of manure cleave phosphoric acid and other ash constituents from organic compounds and use them in the elaboration of their own cells. Stoklasa² has shown also that approximately 25 per cent. of the phosphorus of insoluble phosphates added to media may be assimilated by bacterial cultures in the presence of carbohydrates. The latter author states that as much as 80 per cent. of the phosphorus of bacteria may occur in the form of nucleic acid. If these statements are reliable, the consumption of soluble phosphorus by bacteria might explain the depressions observed in the present work. This possibility is

apparently strengthened by the work of Wüthrich and von Freudenreich,³ who found great numbers of bacteria in the fresh feces of herbivora; and by the work of MacNeal and others,² who found that the bacterial cells of fresh human feces might amount to 50 per cent. or more of the total dry matter. It must be borne in mind also that bacterial counts upon fermenting manure by the usual plating method, while indicating a rapid increase of flora, do not measure the extensive accumulation of dead or inert bacterial cells which must occur.

In view of the preceding observations an experiment was planned in which the action of bacteria could be eliminated and the results compared with those of a normal fermentation. The usual extractions were supplemented by the use of a saturated solution of carbon dioxide (at room temperature) as a solvent to determine its efficiency with actively fermenting manure.

EXPERIMENT WITH ANTISEPTICS

On April 15, 1911, three 25-pound samples of the usual mixture of manures were prepared and mixed with floats³ in the proportion and manner previously followed. One sample was allowed to ferment nor-

mally. To a second sample, 250 cc. of chloroform were added and thoroughly incorporated. The third sample was treated with a similar amount of 40 per cent. formalin. Care was taken to maintain an excess of these antiseptics in their respective samples, the purpose being to inhibit only multiplication of bacteria in the second sample while in the third sample the suppression of bacteria and probably of enzymes should be complete. The samples were stored in pails and weighed at samplings to follow the losses of dry matter. Bacterial counts were made as a check upon conditions favoring fermentation. N/5 nitric acid was used only at the last extraction. The samples for extraction with carbon dioxide were taken simultaneously with those for extraction with water, transferred to sealed Mason jars, treated with a few cc. of chloroform, refrigerated and extracted on the following day. The data of this experiment are given in Table III.

¹ *Centrib. Bakt.* (1895), Abt. II, 1, 873.

² *Jour. Infect. Diseases*, 6, No. 2, p. 123.

³ The sample of floats used here contained 31.62 per cent. total P_2O_5 .

¹ *Lafar's Handbuch d. Tech. Mykol.*, 3, 429.

² *Centrib. Bakt.*, etc., Abt. II, 29, 400

A study of Table III shows that the water-soluble phosphorus of the normally fermenting mixture decreased during 80 days by 15.6 per cent. of the total and 47.2 per cent. of the amount soluble at the beginning. The corresponding losses in mixtures 2 and 3 were 4.5 per cent. and 2.6 per cent. of the total, and 13.8 per cent. and 8.8 per cent. of the originally soluble phosphorus of the respective samples. The data indicate that this readily soluble constituent of manure-floats mixtures is seriously reduced by the process of fermentation but remains practically constant when fermentation is inhibited. Samples Nos. 1 and 3 show losses of 23.1 per cent. and 2.4 per cent. of the phosphorus originally available in the respective cases. It would be difficult to explain why the single figure for availability in sample No. 2 fails to agree with the corresponding figure for sample No. 3, also treated with an antiseptic, but even the latter sample shows a decrease at the second analysis. The bacterial counts and losses of dry matter seem to indicate that this condition cannot be due to reactions accompanying the development of bacteria.

In sample No. 3 the water-soluble phosphorus was lower throughout than in sample No. 1 at the first stage and in sample No. 2 at corresponding dates of analysis. This condition may have been due to a coagulating or hardening action of the formalin upon the organic matter surrounding the otherwise soluble phosphorus compounds, which reduced the effectiveness of the solvent. $N/5$ nitric acid was more efficient than in earlier experiments, the added extraction with this solvent recovering all the phosphorus of sample No. 3 and all but 5.3 per cent. and 8.2 per cent. of the total phosphorus in samples Nos. 1 and 2, respectively, at the close of the experiment.

Comparing the efficiency of carbon dioxide solution with that of water, one finds the results less consistent for the former than for the latter solvent. The irregularities may have been due to changes occurring in the samples while standing previous to extracting. The fact that the efficiency was generally lower for the carbon dioxide than for the water seems to indicate that with these samples conditions were quite different from those obtaining where the solvents were compared upon floats alone or on manure-floats mixture at the extreme stage of fermentation represented in Table II. In harmony with the results from extraction with water, the data for carbon dioxide extracts give evidence of marked suppression of soluble phosphorus where fermentation and bacterial increase proceed freely, as in sample No. 1. These results agree with those of Egorov,¹ who found greater decreases of soluble phosphorus in normally fermenting manure than in manure treated with toluol. Considering the results of this experiment in relation to the two specific points which it was to cover, it appears that the development of bacteria is closely associated with a decrease of water-soluble phosphorus and that the phosphorus of fermenting manure-floats mixtures is not appreciably more soluble in carbon dioxide solution than in water alone.

¹ Loc. cit.

EXPERIMENTS WITH BACTERIA

As a result of the preceding experiment attention was directed to the relation of bacteria to soluble phosphorus in culture media. Mixed flora of manure organisms were grown upon the usual standard agar medium (generally with 0.5 per cent. K_2HPO_4 added). After 2 to 5 days the growths were removed by means of a smooth-edged glass slide, oven-dried and pulverized. These bacterial cells contained 4 per cent. to 8 per cent. of P_2O_5 . A water-extract of bacterial cells from one culture of this sort, obtained in the presence of chloroform and passed through a Pasteur-Chamberland porcelain filter, contained 60.9 per cent. of the total phosphorus of the cells. A similar analysis of the medium from which these cells were obtained showed that it contained 81.9 per cent. of its total phosphorus in water-soluble form. This indicated a depression of 21 per cent. in solubility of phosphorus when assimilated by bacteria from the medium.

Mixed bacteria from manure were grown upon agar media prepared from an extract of fresh manure-floats mixture obtained by squeezing the latter in a heavy press. The phosphorus supply was thus limited to the forms dealt with in the preceding fermentation experiments. Check portions of the media and five-day cultures representing equal amounts of the original media were extracted with water in the presence of chloroform and the extracts were filtered through porcelain. The treatment was thus essentially the same as that applied in the experiments with manures. Two experiments of this sort gave depressions of 40.6 per cent. and 26.5 per cent. of the soluble phosphorus of the media as a result of the growth of bacteria. Since the conditions attending these extractions closely simulated those attending the investigation of manure, it seems reasonable to conclude that bacteria are directly responsible for at least a part of the decrease of water-soluble phosphorus in fermenting manures.

STATUS OF PHOSPHORUS IN THE BACTERIAL CELL

In order to determine whether this effect was due to changes occurring in the medium or to withdrawal of soluble phosphorus from the medium by the bacteria, a study was made of the status of phosphorus in bacterial cells. A few pure cultures but mostly mixed organisms of manure were investigated. The growths were secured from standard media in the manner previously described and incubated 3 days. Water extracts were obtained from fresh intact cells, oven-dried cells and cells dried *in vacuo* over sulfuric acid at room temperature. Other samples of fresh cells were extracted after maceration with glass in a porcelain mortar until microscopic examination showed that practically all the cells had been crushed. This treatment must have eliminated, to a great extent, any protective action exerted against solvents by the cell wall.

Ten grams of fresh cells, or its equivalent in dry cells, were shaken by machine for three hours with 500 cc. of water at room temperature. The extracts were filtered immediately through porcelain. Care

was taken to have chloroform present throughout the work and the filtrates were refrigerated when not analyzed immediately. Phosphorus was determined in 100 cc. aliquots of the filtrate taken at the initial temperature of the solvent, using the Neumann method. It was found that an average of 48.9 per cent. of the total phosphorus in the fresh bacterial cells was soluble in water. Drying did not appear to exert a marked influence on the solubility of phosphorus. In one case water was found to be as efficient when acting upon the fresh, intact cells for 10 minutes as when applied for three hours. This seemed to indicate a possible concentration of soluble phosphorus at the surface of the cell as a result of adsorption from the medium. In view of this possibility determinations of inorganic phosphorus were made on water extracts of several cultures, using the following methods: Hart and Andrews',¹ Forbes',² Emmet and Grindley's³ and Collisons'.⁴

On the whole, there was considerable variation in the results and it must be concluded that they were

the same manner as rock-phosphates for reinforcing farm manure, it seemed desirable to follow the changes of solubility of phosphorus in fermenting mixtures of manure and acid-phosphate and compare the results with those obtained from manure-floats mixtures. On April 6, 1912, a mixture of $\frac{1}{3}$ horse manure and $\frac{2}{3}$ cow manure was put up as follows:

Sample 1. 25 pounds of manure.

Sample 2. 25 pounds of manure + 390 grams acid-phosphate.¹

Sample 3. 25 pounds of manure + 390 grams acid-phosphate + chloroform to saturation.

Sample 4. 25 pounds of manure + 390 grams acid-phosphate + 50 grams CaCO_3 .²

Phosphorus was added in this experiment in a proportion roughly approximating that followed in the rock-phosphate experiments. On the dates indicated in Table IV, the samples were extracted and data obtained in the usual manner. An additional extract was prepared by passing a portion of the usual water extract through Pasteur-Chamberland filters

TABLE IV.—PERCENTAGES OF PHOSPHORIC ACID IN THE DRY MATTER OF CHECK MANURE AND ACID-PHOSPHATE MIXTURES

Sample number and date of analysis	Dry matter in manure, Per cent.	Loss of dry matter, Per cent.	Bacteriological count on gelatin media, millions per gram dry manure	Total P ₂ O ₅ , Per cent.	Water-soluble P ₂ O ₅		Citrate-soluble P ₂ O ₅ , Per cent.	Available P ₂ O ₅		N/5 nitric acid-soluble P ₂ O ₅ , Per cent.	Total soluble P ₂ O ₅		Soluble in filtrate from porcelain	
					Per cent. in sample	Per cent. of total		Per cent. in sample	Per cent. of total		Per cent. in sample	Per cent. of total	Per cent. in sample	Per cent. of total
1. Check manure														
Apr. 6.....	21.70	..	6308	1.93	1.22	63.21	0.53	1.75	90.67	0.05	1.80	93.26	1.12	58.03
July 2 (a).....	14.12	40.3	27	2.62	1.43	54.58	1.18	2.61	99.62	0.07	2.68	102.29	1.30	49.62
2. Acid-phosphate mixture														
Apr. 6.....	23.80	..	5380	3.70	2.03	54.87	1.07	3.10	83.77	0.07	3.17	85.66	1.77	47.80
July 2.....	18.10	32.3	60	4.43	1.47	33.18	2.89	4.36	98.42	0.08	4.44	100.23	1.22	27.54
3. Acid-phosphate mixture + CHCl₃														
Apr. 6.....	23.85	..	6740	3.62	2.10	58.01	1.09	3.19	88.11	0.04	3.23	89.21	1.79	49.40
July 2.....	23.50	0.19	0	3.71	1.26	33.94	2.00	3.26	87.85	0.12	3.38	91.08	1.14	30.73
4. Acid-phosphate mixture + CaCO₃														
Apr. 6.....	24.05	..	9145	3.42	1.30	38.01	1.91	3.21	93.86	0.10	3.31	96.78	1.11	32.50
July 2.....	16.47	44.5	34	4.82	0.95	19.71	4.02	4.97	103.11	0.14	5.11	106.01	0.91	18.88

(a) Period of fermentation = 87 days.

but rough approximations to the actual percentages of inorganic phosphorus. The average of the most consistent figures gave 31.5 per cent. of the total phosphorus as present in inorganic form. The average of water-soluble phosphorus recovered from these cultures was 37 per cent. of the total. From the rough agreement of these percentages it would seem that the greater part of the water-soluble phosphorus of bacterial cells as prepared in this work was derived from inorganic phosphates adsorbed from the medium and concentrated at the surface of the cells. The remaining phosphorus of the cells, which was partly soluble in dilute alkali, probably represented that actually assimilated by the bacteria and presumably existed chiefly as a constituent of nuclein compounds. This condition would be sufficient to account for an appreciable depressing influence of bacteria upon the soluble phosphorus of fermenting manures.

EXPERIMENT WITH ACID-PHOSPHATE

In view of the common use of acid-phosphate in

to insure the removal of bacterial cells. Sample No. 3 was acid in reaction throughout the experiment, while sample No. 2 changed from weakly alkaline to weakly acid. The other samples were distinctly alkaline throughout. Mold growth was especially evident on the surface of sample No. 2 and in the bacterial cultures obtained from this manure. The analytical data are given in Table IV.

The losses of water-soluble phosphorus in this experiment were 8.63 per cent., 21.69 per cent., 24.07 per cent. and 18.30 per cent. of the total phosphorus of samples Nos. 1 to 4, respectively. These values are equivalent to losses of 13.65 per cent., 39.53 per cent., 41.49 per cent. and 48.15 per cent. of the originally water-soluble phosphorus of the respective samples. The phosphorus passing through porcelain filters showed decreases of 14.49 per cent., 43.40 per cent., 37.79 per cent. and 41.91 per cent. from that soluble at the start in the same respective samples. These latter results indicate the presence in the water ex-

¹ Am. Chem. Jour., **36**, 478.

² Ohio Expt. Sta., Bull. **215**, 488.

³ Jour. Am. Chem. Soc., **28**, 35.

⁴ THIS JOURNAL, **4**, 606.

¹ The acid-phosphate was a commercial brand containing 17.7 per cent. moisture, 13.88 per cent. total P_2O_5 and 10.4 per cent. water-soluble P_2O_5 .

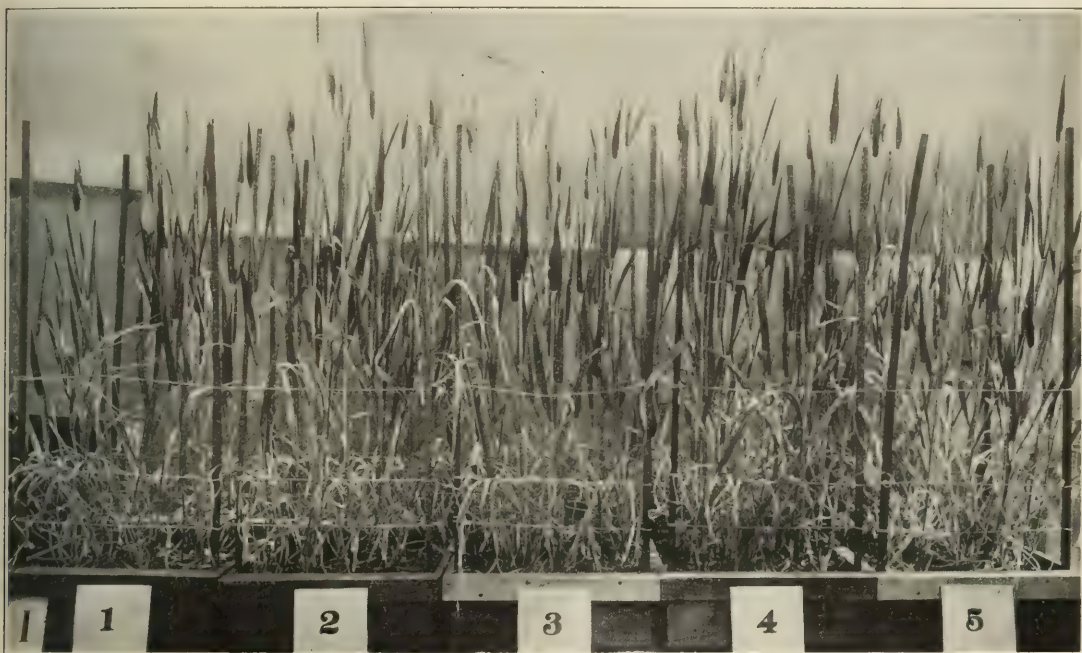
² The calcium carbonate was about twice the amount required to neutralize the acidity of the phosphate as determined by titration.

tracts of only slight amounts of organic or other phosphorus compounds incapable of passing through porcelain filters. The experiment agrees with those described for rock-phosphate, which showed greater depression of solubility in the mixtures than in the check-manure. Moreover, the losses were of approximately the same magnitude as those observed during an equal period of fermentation in earlier work. Sample No. 3, which was subjected to extensive loss of soluble phosphorus in the presence of chloroform, appears to indicate that other factors than bacteria function in the depression of water-soluble phosphorus in fermenting mixtures of manure and acid-phosphate. An absorptive effect of the manure or chemical combi-

presence of acid-phosphate in fermenting manure differ from those obtaining when rock-phosphate is present. In either case several factors may affect the status of phosphorus and the changes appear to be complex.

EXPERIMENTS WITH BARLEY CROPS

As a practical check upon the results already presented it was desirable to know the availability of phosphorus in fermented manure-phosphate mixtures as measured by growing crops. Greenhouse cultures of barley were grown, therefore, upon soil fertilized by manure to which Kahlbaum's c. p. tricalcium phosphate and monocalcium phosphate were added, with the purpose of comparing the influence of fer-



Check
fermented
manure
Box 74

Fermented
manure
+ tri-
phosphate
Box 66

Fermented
manure
+ mono-
phosphate
Box 68

Fermented
triphosphate
mixture
Box 70

Fermented
monophosphate
mixture
Box 72

I. BARLEY CROP No. 1, SET 1, MARCH 29, 1912

nation between the two would seem to be possible factors in the change. The high recovery of phosphorus in available form from the mixtures at the last extraction is a contrast to the results from rock-phosphate and further indicates the effects of such factors as absorption or conversion to compounds soluble in citrate solution. The change was presumably a conversion to dicalcium phosphate in sample No. 4, where an excess of calcium was present. The total soluble phosphorus underwent changes similar to those observed for available phosphorus and the results may be due to the causes suggested for the latter. While this single experiment cannot be considered as giving conclusive results it appears to justify the belief that conditions attending the

menting manure upon soluble and insoluble phosphates. On November 22, 1911, five samples based upon the usual mixture of manures were prepared as follows:

Sample 1. 10 pounds of manure.

Sample 2. 10 pounds of manure + 55 grams tricalcium phosphate.

Sample 3. 10 pounds of manure + 41.5 grams monocalcium phosphate.

Sample 4. 10 pounds of manure.

Sample 5. 10 pounds of manure.

The phosphates supplied equivalent amounts of phosphorus and corresponded to the proportions used in fermentation experiments. On December 22nd, after 30 days of fermentation, 55 grams of tricalcium phosphate were added to sample No. 4, and 41.5 grams

of monocalcium phosphate to sample No. 5. The re-enforced manures were mixed and analyzed for total and water-soluble phosphorus. Table V gives the data.

TABLE V.—PERCENTAGES OF PHOSPHORIC ACID IN DRY MATTER OF MANURE-TRI-PHOSPHATE MIXTURES APPLIED TO BARLEY

Sample	Percentage dry matter in manures	Total P_2O_5 per cent.	P_2O_5 of H_2O ext. passing filter				Bacteria in millions per gram of dry manure	Gelatin media
			Water soluble P_2O_5	Per cent. in manure	Per cent. of total	Per cent. in manure		
1. Check manure	18.95							1098
2. Triphosphate mixture	18.77	5.50	1.22	22.18	0.88	16.00		724
3. Monophosphate mixture	20.82	4.98	2.44	49.00	2.13	42.77		5470
4. Manure + triphosphate	18.55	5.54	1.41	25.45	0.96	17.33		
5. Manure + monophosphate	18.47	5.52	3.25	58.88	2.89	52.36		

Detailed comment upon these results is unnecessary in view of the explanations of preceding tables. The depression of solubility by fermentation was much greater in case of the monophosphate than with the triphosphate; but the soluble phosphorus of the fermented monophosphate mixture was twice as great as that in either of the samples treated with

most striking result of the experiment is the superior yield from monophosphate when applied with fermented manure as compared with its application in the fermented mixture. The effect is more marked with the grain than with the straw.

The availability of the triphosphate, on the other hand, appears to have been influenced but slightly by the action of the fermenting manure. It was also as efficient as the monophosphate applied in the fermented mixture. The equal yields from triphosphate are in harmony with the approximately equal soluble phosphorus in the manures containing it. The monophosphate in the fermented mixture fails to give an increased yield corresponding to its excess of soluble phosphorus over that of the manures containing triphosphate. In the case of the monophosphate, however, the fermented manure plus phosphate contained 20 per cent. more soluble phosphorus than did the fermented mixture and gave an increase of 37 per cent. in yield of grain. The extensive bacterial flora in the fermented mixture of monophosphate would seem to be a possible cause of the low availability observed for that sample. Apparently the soluble phosphorus is retained, possi-

TABLE VI.—WEIGHT IN GRAMS OF AIR-DRY BARLEY OF HARVEST I FROM MANURES REINFORCED WITH PHOSPHATES

Manure applied	Fermented manure + triphos.			Fermented manure + monophos.			Fermented mixture with triphos.			Fermented mixture with monophos.			Check fermented manure		
	Box number	65	66	Average	67	68	Average	69	70	Average	71	72	Average	73	74
Grain.....	20.92	24.82	22.87	26.42	29.92	28.17	19.13	26.96	23.05	17.06	24.02	20.54	21.62	21.16	21.39
Straw.....	35.38	42.18	38.78	42.88	44.18	43.53	33.17	41.84	37.51	35.44	34.18	34.81	39.68	36.84	38.26
Total.....	56.30	67.00	61.65	69.30	74.10	71.70	52.30	68.80	60.55	52.50	58.20	55.35	61.30	58.00	59.65

triphosphate. These manures were applied in duplicate at the rate of 100 grams each to 15 kilograms of uniform clay loam¹ in wooden boxes. Applications were made as follows:

Box No.

65	}	Fermented manure + tricalcium phosphate
66		
67	}	Fermented manure + monocalcium phosphate
68		
69	}	Fermented mixture of manure and tricalcium phosphate
70		
71	}	Fermented mixture of manure and monocalcium phosphate
72		
73	}	Check fermented manure
74		

On December 23rd, the boxes were planted to barley of the variety Oderbrucker No. 6. The crops were thinned to sixteen per box on January 3rd. Several sprayings with atomic sulfur preparation were required to suppress mildew. Smut or stripe-disease rendered sterile 3 plants in box 66 and 2 plants each in boxes 72 and 74. On May 3, 1912, the mature crops were harvested, dried at about 50° C. and allowed one month to attain an air-dry condition. Seed and straw were then separated and weighed. The data are given in Table VI.

The difference in yield of duplicate boxes may have been due to slight differences in the greenhouse environment of the two sets of boxes. They run so nearly parallel, however, that the average yields, apparently, may be considered reliable data. The

¹ The soil contained 0.3 per cent. total and 0.15 per cent. HCl-soluble P_2O_5 on the air-dry basis.

bly by adsorption, in a form readily recovered by water and yet assimilated with difficulty by the roots of the barley plant. The yields of straw show the same general relations as those of grain.

A second crop of barley was planted in the soils of the previous experiment on May 8th. Chevalier barley was chosen on account of its resistance to mildew, and the selected seed was treated with formalin in the usual manner to destroy smut spores. The plants were thinned to 16 per box on May 21st. They were free from disease throughout growth. Nitrogen and potassium were liberally supplied to the odd-numbered set of boxes in the hope to make phosphorus the chief factor limiting fertility but these crops failed to produce seed and the yields are omitted. The normal crops were harvested on August 13th and cured as before. The data are given in Table VII.

TABLE VII.—WEIGHT IN GRAMS OF AIR-DRY BARLEY OF HARVEST II FROM MANURES REINFORCED WITH PHOSPHATES

Manure applied to crop of harvest I	Fermented manure + triphosphate		Fermented manure + monophosphate		Fermented mixture with triphosphate		Fermented mixture with monophosphate		Check fermented manure
	Box number	66	68	70	72	74			
Grain	3.31	3.38	4.07	3.75	0.51				
Straw	14.49	14.12	14.23	14.55	16.79				
Total	17.80	17.50	18.30	18.30	17.30				

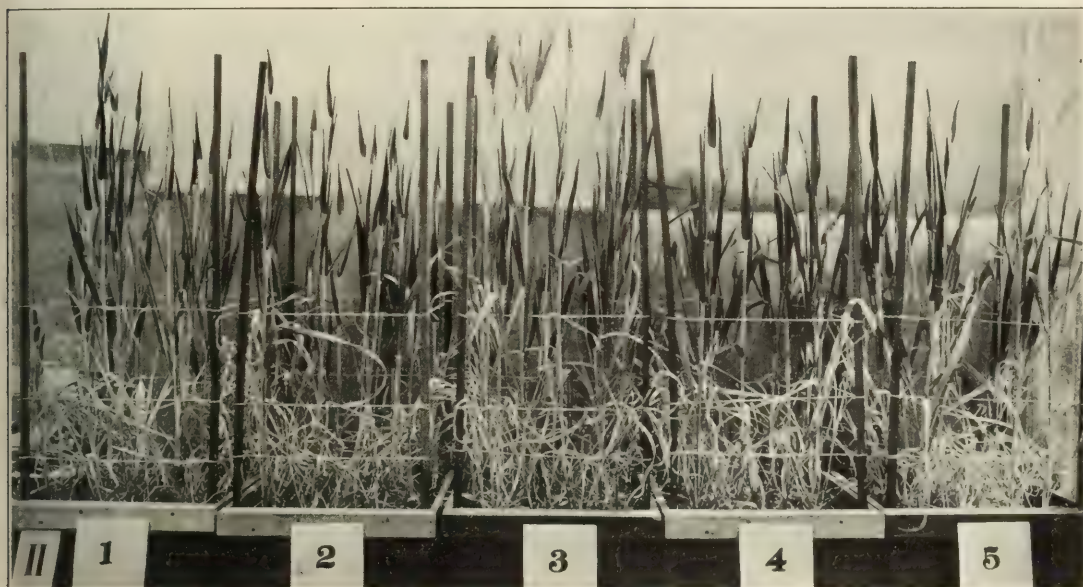
In this second harvest from the original application of manures the triphosphate of the fermented

mixture gave 23 per cent. more yield of grain than did triphosphate added to fermented manure. Monocalcium phosphate showed a complete reversal of efficiency from that recorded for the first harvest. In harvest I the freshly added phosphate gave an increase of 37 per cent. in yield of grain over the fermented mixture while in harvest II the yield of grain from the fermented mixture was 11 per cent. greater than from the fermented manure with freshly added phosphate. The results indicate increasing availability of the phosphorus in the fermented mixtures with duration of exposure in the soil.

Determinations were made of the amounts of phosphorus removed from the odd-numbered set of boxes by harvest I, using the official method of incineration with $\text{Mg}(\text{NO}_3)_2$. The results showed only

of P_2O_5 content from which the availability of the soil supply can be interpreted. If this be true, the preceding results indicate that the phosphorus of soluble and insoluble calcium phosphates was equally available after prolonged contact with fermenting manure. Phosphorus of triphosphate appears to have been equally, if not more, available after contact with fermenting manure than when applied with manure previously fermented.

In the case of monophosphate higher availability was shown by the manure reinforced at the time of application than by the fermented mixture. The results agree with the yields of crop produced. On the basis of total P_2O_5 assimilated the manures showed increasing efficiency in the following order: fermented manure + triphosphate, fermented mixtures of



Check
fermented
manure
Box 73

Fermented
manure
+ tri-
phosphate
Box 65

Fermented
manure
+ mono-
phosphate
Box 67

Fermented
triphosphate
mixture
Box 69

Fermented
monophosphate
mixture
Box 71

II. BARLEY CROP NO. 1, SET 2, MARCH 29, 1912

slight variations (from 0.9 per cent. to 1.08 per cent.) of P_2O_5 in the air-dry grain crops. The P_2O_5 content of the air-dry straw was 0.16 per cent. in the crops from check manure and fermented mixtures, 0.12 per cent. from fermented manure + triphosphate and 0.21 per cent. from fermented manure + monophosphate. Calculations based on yields and P_2O_5 content show that the following weights in milligrams of P_2O_5 were assimilated from the boxes indicated:

Check manure (box 73) 288; fermented manure + triphosphate (box 65) 229, + monophosphate (box 67) 354; fermented mixture with triphosphate (box 69) 246, with monophosphate (Box 71) 241.

According to Hall¹ barley straw shows variations

¹ "The Soil," second edition, p. 156.

mono- and of triphosphate, check manure and fermented manure + monophosphate.

It is manifestly unsafe to draw conclusions from the preceding experiments with pure phosphates and apply them to commercial materials, such as rock-phosphate and acid-phosphate. It would seem reasonable, however, to expect the same general conditions to obtain for both classes of phosphates and that, consequently, acid-phosphate will give the highest immediate returns when withheld from contact with fermenting manure until the latter is applied to the soil. Rock-phosphate may be expected, apparently, to give the same immediate returns whether applied in fermented mixture or simultaneously with fermented manure. Succeeding crops, however, ought to give superior results from fermented mixtures; and this condition

agrees with the delayed action of rock-phosphate frequently observed in field practice.

While this investigation has indicated that complex relations exist between fermenting manure and reënforcing phosphates, it seems also to have indicated reasons which may explain the results and correlate them with observations from farm practice. It may be stated that, apparently, bacteria are a direct and important factor in depressing the soluble phosphorus of fermenting mixtures of manure and rock-phosphate. This effect seems to be due chiefly to the formation of insoluble nuclein compounds in the bacterial cell. When acid-phosphate is added to manure there is a depression of soluble phosphorus, even when the development of bacteria is practically inhibited. This result is apparently due to absorption of the phosphate by the manure.

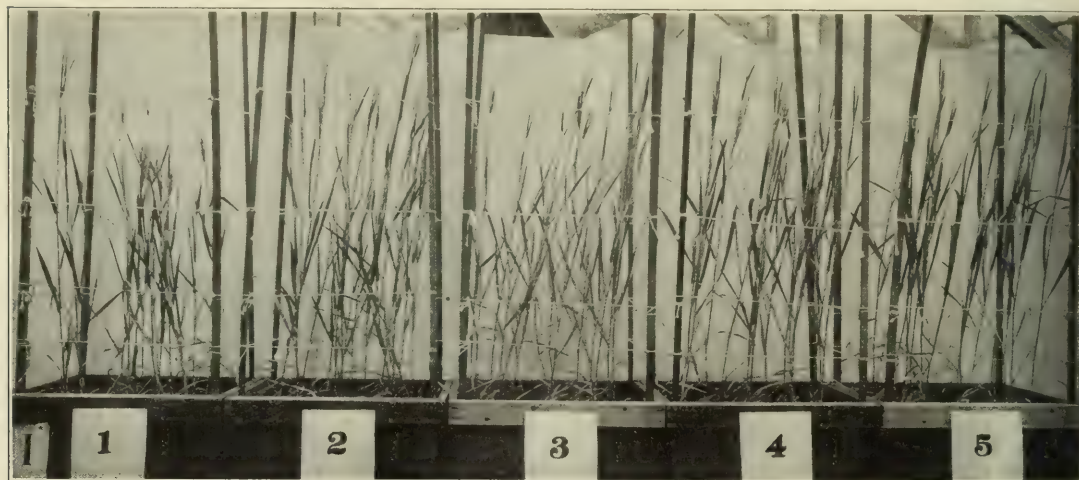
In the case of rock-phosphate these changes appear to have no significant influence upon immediate re-

ously its efficiency for immediate returns of crop. The indications are that it is inadvisable to allow prolonged contact of this phosphate with manure in a fermenting mixture. For reënforcing purposes it seems best to add it to the manure when the latter is applied to the soil.

SUMMARY

Fermentation over periods of four to six months caused a decrease of water-soluble phosphorus in manures and mixtures of manures with rock-phosphate. The losses were greatest in the mixtures, where they amounted to more than one-half the soluble phosphorus originally present. Ammonium citrate solution and $N/5$ nitric acid did not recover this depressed phosphorus in all cases and hence other changes than simple reversion to insoluble phosphates apparently occurred.

Ammonium carbonate solution of the strength existing in the moisture of fermenting manure was no



Check
fermented
manure
Box 74

Fermented
manure + tri-
phosphate
Box 66

Fermented
manure + mono-
phosphate
Box 68

Fermented
triphosphate
mixture
Box 70

Fermented
monophosphate
mixture
Box 72

III. BARLEY CROP NO. 2, SET 1, UNFERTILIZED, JULY 19, 1912

turns of crop. Either the phosphorus affected by fermentation is as readily available as that of the phosphate, or the phosphate unaffected meets the demands of the crop as efficiently as the original supply. When a second crop is grown the phosphorus involved in fermentation of the mixture is apparently more available than that of the phosphate added to fermented manure. This condition may explain the delayed efficiency of rock-phosphate observed in field practice. It probably results from the action of soil organisms and other factors by which the bacterial cells of the manure are destroyed and the absorbed and assimilated phosphorus is liberated in forms available to the crop. The final result is apparently advantageous.

In the case of acid-phosphate the apparent effect of contact with fermenting manure is to reduce seri-

ously its efficiency for immediate returns of crop. The indications are that it is inadvisable to allow prolonged contact of this phosphate with manure in a fermenting mixture. For reënforcing purposes it seems best to add it to the manure when the latter is applied to the soil.

A saturated solution of CO_2 was not superior to water as a solvent for phosphorus in manures and mixtures which had fermented about two and one-half months, and in which bacteria were active, but was superior when fermentation had covered ten months and the bacteria had become practically inert. It was five times as efficient as water or the ammonium carbonate solution in solvent power for phosphorus of rock-phosphate.

The addition of either chloroform or formaldehyde, which practically inhibited bacterial action, greatly reduced the losses of water-soluble phosphorus in mixtures of manure and rock-phosphate.

Dry bacterial cells of manure organisms grown on

agar media contained four to eight per cent. P_2O_5 . The growth of manure organisms upon media supplied with the soluble phosphorus of fresh manure-rock phosphate mixtures depressed the water-soluble phosphorus of the media by amounts which were comparable to the losses of water-soluble phosphorus observed in fermenting manures. About one-half the phosphorus of fresh intact bacterial cells was soluble in water. This phosphorus was apparently derived chiefly from inorganic phosphates adsorbed from the media. The remaining phosphorus of the cells was probably present in nucleic compounds.

Acid-phosphate incorporated with fermenting manure underwent essentially the same changes of solubility as did rock-phosphate. In the presence of chloroform, however, the acid-phosphate decreased markedly in solubility, while with rock-phosphate no decrease occurred.

Application of monocalcium phosphate to barley in pot experiments gave greater immediate returns when the phosphate was applied with previously fermented manure than when it was applied in a fermented mixture of manure and phosphate. The immediate returns from tricalcium phosphate were the same whether it was applied with previously fermented manure or in a fermented mixture. A second crop of barley from the original application of reinforced manures gave a superior yield from the fermented mixture for both phosphates.

The conclusions derived from this work require confirmation under field conditions before they can be applied to direct agricultural practice. However, so far as pot experiments indicate conditions in field practice, the final results from mixing rock-phosphate with fermenting manure appear to be advantageous. In the case of acid-phosphate it appears inadvisable to mix the material with fermenting manure. It is probably better practice to add it to the manure at the time of application to the field.

The authors desire to express appreciation to Professor E. B. Hart for helpful suggestions and criticism received during this investigation. The results will appear in detail as a technical bulletin from the Wisconsin Experiment Station.

AGRICULTURAL CHEMISTRY AND BACTERIOLOGY LABORATORIES
WISCONSIN EXPERIMENT STATION
MADISON

THE GAY-LUSSAC METHOD OF SILVER DETERMINATION¹

By FREDERIC P. DEWEY²

Received November 19, 1912

This old and well-known method of determining silver is, in bullion work, so far superior to the furnace assay that it is looked upon with reverential awe by many, if not by most, users, and its ease of execution with proper equipment commends it highly where much commercial bullion work on silver is required.

The method is so thoroughly well known that a description of it here may seem to be unnecessary, but many thousand determinations are annually

made by it in the United States Mint Service and its practice is there reduced to an art. This is necessary both for the sake of economy of time and because high-grade work with it requires constant practice. It is useless for a person who uses it only occasionally to expect to attain high accuracy with it, without spending more time upon a determination than is warranted in a busy commercial laboratory.

It is always employed in the Mint service whenever possible, but its chief field is in the determination of silver in standard silver (ingots and coin), which is 900 fine in silver and 100 fine in copper, and I shall first briefly outline its use on this metal and then take up various points in detail, especially as related to the accuracy of the results obtained.

For this determination 1115 milligrams of standard metal are weighed and transferred to a glass-stoppered bottle, the metal is dissolved in nitric acid and 100 cc. of a standard solution of NaCl run in. The bottle is then vigorously shaken and a measured portion of a decimal salt solution added. The bottle is again shaken, more decimal solution added, and again shaken, if necessary. These operations are repeated until the silver is precipitated.

Standard metal being 900 fine, 1115 mg. should carry 1003.5 mg. of silver, which is a convenient figure to work by. Legally, standard metal may vary 3 in fineness above or below 900. Practically, however, it seldom runs below 898 or above 901 fine. Therefore, the variation in actual silver present above or below 1003.5 mg. is not excessive. For testing the standard salt solution we weigh up 1004 mg. of proof silver. For convenience and accuracy we have single weights of 1115 mg. and 1004 mg.

The bottles should be of perfectly white glass, carefully made and well annealed; 8 oz. is a convenient size often used, the bottles are most conveniently handled in a circular frame or basket, holding ten. For dissolving the silver, both the amount and strength of nitric acid used may vary considerably without apparent effect upon the accuracy of the results, 8 cc. at 1.30 sp. gr. to 25 cc. at 1.20 sp. gr. being allowable. Some operators heat the bottles to remove nitrous fumes, others do not.

The standard salt solution is designed to have 100 cc. precipitate exactly 1 gram or 1000 mg. of silver, but it seldom "shows" this exact strength. The word "shows" is used instead of "is" because the equivalent of the solution depends upon other factors besides its composition.

In general, two proofs should be used in every set of 10 bottles, unless several sets are to be run in rapid succession, when one proof in each set may answer. Some operators run an independent proof occasionally during the day and omit the proofs in the sets, but this proceeding is objectionable.

The next step in the method is the addition of 100 cc. of the standard salt solution (often improperly called "normal" salt solution). This is a very simple operation, but it requires the utmost care and constant attention to details if high accuracy is desired in the results. Only a minute variation in the

¹ Published by permission of the Director of the Mint and jointly with the American Institute of Mining Engineers.

² Assayer, Bureau of the Mint.

amount of solution added will make a serious variation in the fineness of silver shown.

The Stas pipette is the one universally used in the Mint service. It is a simple pipette open at both ends and securely mounted on a wall bracket. The upper end is drawn out to a fine opening and is provided with a collar-cup to catch the drip. The lower end is comparatively large and must have a free and smooth discharge. The lower end is connected through a removable rubber tube, provided with a pinchcock, with an elevated tank containing the salt solution. No stopcocks, floats, or graduations of any kind can be used on or in the pipette if rapid work is to be done. It is also questionable if any such arrangement can be as accurate as the simple filling of the Stas pipette and letting its contents run directly into the silver bottle.

In operating the Stas pipette the rubber tubing is slipped over the lower end and the pinchcock opened. As soon as the solution comes out of the upper end of the tube, it is closed by the first finger of the left hand and the pinchcock closed. The operator must now be sure that there are no air bubbles in the pipette. If such should appear they must be allowed to collect at the top of the pipette; the pinchcock must be opened, the finger momentarily removed from the upper end of the pipette, and the pinchcock closed again. When the pipette is full of solution and the pinchcock closed, the rubber tube is withdrawn from the lower end of the pipette. This end must now be carefully examined to see that there is no surplus solution adhering to it or that the air has not commenced to ascend the tube.

If the lower end of the tube is in proper condition the silver bottle is now placed directly under it, the finger removed from the upper end and the solution allowed to flow into the bottle. The solution should flow out rapidly in a smooth, solid stream. Just as soon as the flow stops, the bottle must be removed from under the pipette. It is absolutely fatal to accuracy to attempt any adjustment of the drip of the pipette. There should be only just easy clearance between the bottom of the pipette and the top of the bottle.

The pipette is supposed to contain 100 cc. and on various accounts it is desirable that it should be fairly accurate, but it is not at all necessary that it should be absolutely accurate. The absolutely essential point about it is that it should deliver exactly the same amount of solution to each one of the ten bottles composing a set. The amount delivered may be a trifle more or a trifle less than 100 cc. or it may vary slightly from a hot day in summer to a cold day in winter, but it should not vary between the first and last bottles of a set. It is a good plan to fill and empty the pipette a few times before beginning to fill the set. After withdrawing the bottle from under the pipette the stopper is dipped in distilled water and inserted into the neck of the bottle with care.

Having filled the set, the carefully stoppered bottles are placed in a shaking machine and agitated for 3 to 5 minutes to settle the precipitate. The bottles are next placed upon a black shelf, technically called

a "board," with a black background about as high as the shoulder of the bottle and about 3 inches back of the bottle, the whole being installed in a window, preferably with a northern exposure.

Up to this point in the method, the procedure is substantially the same in all the laboratories, but from here on there are slight differences in the manipulations. In common with many volumetric methods, there is difficulty in this one in determining the end point. In many descriptions of the method the operator is directed to add decimal salt solution in small measured amounts, with agitation between the additions, until no more precipitate is formed on adding the salt solution. Too much salt has now been added and this excess must be determined by the addition of small measured amounts of decimal silver solution and the amount of silver present in the metal determined by balancing these amounts.

This method is open to two serious objections. When exactly the proper amount of salt has been added to precipitate the silver present, a condition of equilibrium in the solution results, which is disturbed by the addition of either reagent with the separation of a precipitate. This obscures the end reaction. These alternate dosings and shakings consume too much time for rapid work, and after many shakings the solution does not clear well.

In the Mint service, therefore, the operation known as "reading the cloud" has been substituted for these alternate dosings of the solution. This operation is far more rapid, but it requires a great deal of skill and constant practice to yield the best results. In reading the cloud, after the addition of the 100 cc. of standard salt solution and shaking, a measured amount, 1 or $\frac{1}{2}$ cc., of decimal salt solution is added to each bottle. The delivery end of the pipette is placed against the neck of the bottle as far down as possible and the solution allowed to flow gently down the side of the bottle so that it will remain on the surface of the solution in the bottle with the minimum amount of mixing; by a slight rotary motion of the hand the decimal solution is then mixed with the upper portion (about $\frac{1}{3}$) of the bottle solution. This produces a cloud of AgCl in the solution and the next step is based upon the appearance of this cloud. Here the skill and visual condition, together with the personal equation, of the operator are of the utmost importance.

If the cloud be very heavy two or more portions of decimal salt solution are added, the amount depending upon the density of the cloud, and the bottles shaken in the machine again. If the cloud is light, only one dose of decimal is used. If the cloud is very light the bottle is again shaken by hand to bring more of the solution into reaction and the cloud again examined. As the result of this treatment one dose of decimal may be used, or the bottle may be shaken by hand again to bring the balance of the solution above the precipitate into the reaction. Here again a dose of decimal may be used, or the final reading of the cloud may take place. In the final reading the operator estimates from the density of the cloud what portion of the dose of decimal solution was consumed in pre-

precipitating the silver. Many operators estimate to 0.25 cc., others claim to be able to estimate to 0.1. The results of the investigation given beyond indicate that on standard metal estimating to 0.1 is not profitable under present conditions.

All the bottles are eventually brought down to the final cloud, and at the end the amount of decimal solution added to each bottle is recorded. The records of the assays are then compared with the proofs and the fineness of the samples determined. The actual fineness of a sample is shown entirely by the amount of decimal solution used as compared with the amount of decimal required by the proof. It is entirely independent of the amount of standard solution used. Therefore in determining the fineness of a sample we simply compare the amount of decimal used with the amount used in the proof, making allowance for the 0.5 mg. more of silver in the proof above the silver in 1115 mg. of metal at the exact standard of 900, and taking into consideration the weight of the sample used. For instance, if the sample required 0.5 cc. less than the proof, the sample would be reported at 900. This is not strictly exact because 0.25 cc. of decimal salt solution equals 0.25 mg. silver, but 0.25 mg. is only 0.22 fine on 1115 mg. and 0.5 cc. would be only 0.44 fine. However, this variation is too slight for practical consideration, and in general the finenesses are read directly from the difference between the sample and proof. Generally also, the differences are read in quarters of a cc.

Practically we deduct $\frac{1}{4}$ from the amount of decimal solution used on the proof and call it standard. Then for each quarter's difference from standard we add or subtract, as the case may be, from 900 in accordance with the following tabulation:

For 1/4.....	0.2	For 6/4.....	1.3
For 2/4.....	0.4	For 7/4.....	1.5
For 3/4.....	0.7	For 8/4.....	1.8
For 4/4.....	0.9	For 9/4.....	2.0
For 5/4.....	1.1	For 10/4.....	2.2

A second method of determining the end point, which appears to be even more exact, but which requires more time, consists in adding only 0.25 cc. of the decimal solution after machine shaking, then estimating the number of quarters the solution will stand. These are added and the bottles shaken in the machine. This is continued until the quarter added after shaking produces no precipitate, in which case the last quarter is not counted, or else such a slight precipitate is produced that the quarter is counted but the bottle is not shaken again. The reading of the results is the same as before described.

In both these methods great care is exercised to avoid the addition of so much salt as to require back-titration with decimal silver. Back titration is regarded with much disfavor.

In the regular work of the Mint Bureau it became desirable to ascertain just how much reliance could be placed upon the results obtained by the Gay-Lussac method as ordinarily executed in the service and an extensive investigation was undertaken for this purpose.

Six samples, representing three melts of ingots, were

distributed among four laboratories in the service without informing any of the institutions just what the samples were. Table I summarizes the results reported:

TABLE I—ASSAYS OF THREE INGOT MELTS

Fineness	No. 1		No. 2		No. 3	
	A	B	A	B	A	B
898.3			1			
898.4	2	1	2	2		1
898.6	2	4	2	2	3	2
898.7			1			
898.8			2	1		
898.9	5	5	5	5	6	6
899.0			2			
899.1	10	9	8	7	8	7
899.2		1			2	1
899.3	1	1				
899.4					1	1
899.5					1	1
899.6				2		
Total ...	20	21	21	21	21	19

Notwithstanding the great preponderance of results from 898.9 to 899.1 shown here, the ingot melts were reported by the assayer of the mint where they were made as follows:

No. 1 898.5 fine in silver
No. 2 898.25 fine in silver
No. 3 898.5 fine in silver

This table was submitted to the various assayers for criticism and comment and suggestions for improvements in the method. Five reasons were advanced to explain, in part at least, the differences shown in the table, as follows:

- (1) Difference in samples taken for assay.
- (2) Non-homogeneity of the metal.
- (3) Working on a sample on different days.
- (4) The personal equation of the operator.
- (5) Accidents.

Two assayers suggested that perhaps under the actual, every-day working conditions of our service, the method is not so accurate as it is supposed to be.

It was quite impossible at this time to deal with the personal equation of the operator or the chapter of accidents, but, in order to meet the first two of these reasons, a small bar of standard silver was prepared in the Bureau laboratory with especial care to avoid segregation of the metal. It was then rolled out and cut into small oblongs, of which 30-35 were required to weigh 1115 mg. To meet the third reason, four samples of the oblongs, each weighing approximately

TABLE II—ASSAYS OF 22 SAMPLES OF A SMALL BAR OF STANDARD SILVER

3 assays showed 899.1	} fine in silver	
6 assays showed 899.3		
6 assays showed 899.5		
10 assays showed 899.6		
1 assays showed 899.7		
4 assays showed 899.8		
7 assays showed 899.9		
14 assays showed 900.0		
2 assays showed 900.1		
4 assays showed 900.2		
8 assays showed 900.3	}	
1 assay showed 900.4		
—	60	

3.75 grams, sufficient for three determinations of the silver, were sent to each one of the same four laboratories at one time. Subsequently, one laboratory ran

two more samples. In all 66 assays were made and practically all of the bar was used for these assays. Table II summarizes the results reported.

This table was also submitted to the four assayers for comment and criticism, and the investigation was continued upon six sets of ingot samples and six special samples. These samples were sent out to the four institutions for comparative test assays, in a long series. In no case was any institution informed as to the source of the metal, or given the results of any previous assays. The samples were sent out in lots of four in all cases but one. In several cases all four samples in a lot were the same and in two cases this fact was stated in sending them out. In many cases two or three samples in a lot would be the same, but this fact was not disclosed. In one case six samples,

there might be some slight difference in the samples themselves. The two following tables, however, indicate that in the present condition of the method such differences would be masked by differences in the results due to the method itself.

The regular samples from a melt of ingots are generally too small to allow a sufficient number of test assays to be made. From three melts one mint supplied larger samples and they were sent to the four laboratories for test assays and Table III summarizes the results reported, together with the original assays made at the mint of origin of the samples.

This table indicates that there was a very decided tendency at this mint to report their ingots high.

Another mint supplied two sets of ingot samples that were sent out to the four laboratories in the general series of samples, and Table IV summarizes the results reported and gives the original assays made at the mint:

TABLE III—ASSAYS OF THREE MELTS OF INGOTS
Melt No. 132

Fineness	Original assays				Test assays				Total
	Mint of origin		Mint of origin		Independent				
	A	B	A	B	A	B			
898.3			2	1	1	1		5	
898.4					2			2	
898.5						1		1	
898.6			1	2	3	4		10	
898.7									
898.8									
898.9					3	9		12	
899.0									
899.1	1	1	3	1	2	2		8	
899.2									
899.3						3		3	
899.4									
899.5	1	1		2	2	2		6	
Total.....	2	2	6	6	13	22		47	
Report 899.3									
Melt No. 133									
898.3				1	2	1		4	
898.4					3	1		4	
898.5					2	1		3	
898.6	1		6	2	8	5		21	
898.7									
898.8									
898.9					3	4		7	
899.0						1		1	
899.1	1	1		2		4		6	
899.2									
899.3						1		1	
899.4									
899.5				1				1	
900.0		1							
Total.....	2	2	6	6	18	18		48	
Report 899.1									
Melt No. 138									
898.6					9	2		11	
898.7									
898.8					1			1	
898.9					4	7		11	
899.0					2	2		4	
899.1	1		6	6	2	5		19	
899.2						1		1	
899.3									
899.4									
899.5	1	2							
Total.....	2	2	6	6	18	17		47	
Report 899.5									

representing the three regular samples of a melt of ingots, were sent out with this statement, but it was not shown which were the duplicate samples.

In the ordinary operations of melting ingots and taking samples from the melts, it is quite possible that

TABLE IV
Melt No. 175

Fineness	Original assays			Test assays									Total
	Mint of origin			Mint of origin			Independent						
	A	B	C	A	B	C	A	B	C				
898.4							1					1	
898.5													
898.6				1								1	
898.7													
898.8													
898.9				5	1							6	
899.0							1					1	
899.1		1			2			2	1			5	
899.2							1					1	
899.3	1	1	1		3	1	3			2		9	
899.4													
899.5						1	8	7	1			17	
899.6	1		1								3	3	
899.7						2	1	2				5	
899.8							3	3	4			10	
899.9					2							2	
900.0									1	5		6	
900.1													
900.2													
900.3													
900.4									2	2		4	
Total....	2	2	2	6	6	6	18	17	18			71	
Report 899.3													
Melt No. 176													
898.9				3	3	3						9	
899.0													
899.1				1		3				1		5	
899.2													
899.3				2	1	1						2	
899.4													
899.5													
899.6	2	2		1	2		6	2	11			19	
899.7							1		2			6	
899.8							2	3	1			6	
899.9							2	1	1			4	
900.0							1	1				2	
900.1							5	11	2			18	
900.2													
Total....	2	2	2	6	6	6	18	18	18			72	
Report 899.5													

A third set of samples from the second mint was sent out in a set of six and the institutions informed that they represented a melt of ingots, but the duplicates were not indicated; Table V summarizes the results reported, together with the original mint assays:

TABLE V—SAMPLES OF AN INGOT MELT ASSAYED AT ONE TIME
Melt No. 180

Test assays										
Original assays										
Mint of origin			Mint of origin			Independent				
Fineness	A	B	C	A	B	C	A	B	C	Total
899.3		1	1				1			1
899.4								1	2	3
899.5							6	5	9	20
899.6	2	1	1					1		1
899.7								1	1	2
899.8				2	1		4	5	4	16
899.9							3	2		5
900.0				6	4	5	3	2	2	22
900.1							1	1		2
Total....	2	2	2	6	6	6	18	18	18	72
Report 899.5										

The general tendency of the original reports on these three melts appears to be a trifle low, and this is supported by the low test assays on melt No. 176, made at the mint of origin.

In the last three tables all the results reported have been given. Undoubtedly, some of these were vitiated by accidents. These tables also indicate that there is a general laboratory equation similar to the personal equation of an operator.

In order to eliminate differences in the samples as a source of difference in the assay results, one mint prepared two special samples in regard to which the assayer wrote: "I have prepared two samples of standard silver (6 oz. each). I used coin ingot melted a number of times with stirring; finally cast in a closed mold that had been chilled with ice; poured silver at as low temperature as possible. Resulting bars were very free from oxidation. They were, however, thoroughly cleaned, and rolled into strips and cut."

The samples cut into oblongs, of which it took about 30 to weigh 1115 mg., were forwarded to the Bureau, where they were further mixed and portions

TABLE VI—ASSAYS OF TWO SPECIAL BARS

Original assays			Bar No. 1. Test assays			
Fineness	Mint of origin	Mint of origin	Lab. No. 1	Lab. No. 2	Lab. No. 3	Total
898.4		6	3			9
898.5			2			2
898.6	10	18	11	19	20	68
898.7			8			8
898.8			1			1
898.9		6		11		17
899.0						
899.1			2		6	8
Eliminated			3		4	7
Total.....	10	30	30	30	30	120
Bar No. 2						
898.4	1	5	4			9
898.5			4			4
898.6	5	14	12	14	12	52
898.7			2			2
898.8			3			3
898.9	4	7	1	13		21
899.0			1			1
899.1				3	15	18
Eliminated		4	3		3	10
Total....	10	30	30	30	30	120

of 3.75 grams weighed out into small envelopes, giving ample material for three determinations of silver in each envelope. Ten envelopes were sent at various times to each one of the four institutions. Each

laboratory made 30 determinations of silver on each of the larger samples, making a total of 120 assays on each, but in tabulating the results reported a certain amount of discretion has been exercised. In general, results at either extreme in fineness have not been included in the table unless they were reported at least twice by two laboratories, or five times by one laboratory; Table VI summarizes the results, together with the original assays at the mint of origin.

Another mint (Lab. No. 3 above) prepared two special granulation samples in regard to which the assayer wrote: "I am submitting two samples of six ounces each of the most homogeneous standard silver that I have been able to prepare. These samples were prepared as follows: Standard silver ingot granulations assaying from 899.1 to 899.8 and weighing in the aggregate a little over 30 ounces were melted with frequent stirring and the entire melt granulated. Two samples of about 8 ounces each were then segregated and 18 assays made from different portions of the sample. Seventeen of these assays went 899.5."

These samples were divided into portions weighing 3.75 grams each, at the Bureau. It was not noticed at first that they were really only one sample so that 11 envelopes of No. 1 and 9 envelopes of No. 2 were sent to each one of the four institutions. Table VII summarizes the results reported, together with the original assays at the mint of origin.

TABLE VII—ASSAYS OF SPECIAL GRANULATIONS

Original assays			Test assays			
Fineness	Mint of origin	Mint of origin	Lab. No. 1	Lab. No. 2	Lab. No. 3	Total
Portion No. 1						
898.6			8	8	1	17
898.7			6			6
898.8			5			5
898.9			3	13	13	29
899.0			3			3
899.1		10	1	12	12	35
899.2			2			2
899.3			2		6	8
899.4						
899.5	17	23	1		1	25
Eliminated	1		2			2
Total...	18	33	33	33	33	132
Portion No. 2						
898.6		2	11	5		18
898.7			5			5
898.8			7			7
898.9			3	7	12	22
899.0						
899.1		9		15	14	38
899.2						
899.3					1	1
899.4						
899.5	17	16	17			17
Eliminated	1					
Total...	18	27	27	27	27	108

In this case Lab. No. 3 is the one that supplied the special bar samples. The laboratory supplying these special granulation samples is the same one that forwarded ingot samples Nos. 132-3-8, and the same tendency to obtain high results is again shown here.

More than 15 years ago, in an article entitled "The Actual Accuracy of Chemical Analysis," in speaking

¹ *Trans. A. I. M. E.*, **26**, 370 (1896); *Jour. Am. Chem. Soc.*, **18**, No. 9, p. 808 (Sept., 1896).

of the "degree of accuracy exhibited in actual everyday practice" I said: "In estimating this, little or no weight will be given to the evidence afforded by the agreement of duplicate or multiple determinations by the same chemist, for I am convinced that such agreement is a delusion and a snare." The results reported on these granulation samples afford a striking illustration of the soundness of this position. This metal was assayed 257 times. The laboratory preparing it reported it 56 times at 899.5 fine, but the other laboratories reported this figure only 3 times and one of these determinations was questioned by the laboratory reporting it. On the other hand the work of the other laboratories shows that this metal could not have been over 899 fine.

Another small bar was prepared in the Bureau laboratory with especial care, and cut up into oblongs requiring 30-35 to weigh 1115 mg. These oblongs were thoroughly mixed and small samples of 3.75 grams put into envelopes. Ten of these envelopes were sent to each one of the four institutions and Table VIII summarizes the results reported:

TABLE VIII—ASSAYS BUREAU SPECIAL SAMPLE No. 2

Fineness	Lab. No. 1	Lab. No. 2	Lab. No. 3	Lab. No. 4	Total
899.1		6			6
899.2					
899.3		6	3		9
899.4					
899.5	5		6		11
899.6	4				4
899.7	12				12
899.8			9		9
899.9	6				6
900.0	2	13	9	17	41
900.1					
900.2		5	3		8
900.3					
900.4	12			13	25
Total.....	30	30	30	30	120

The laboratories here are numbered the same as in Table VII, and No. 4 is the mint of Table VII.

A final sample was made up at the Bureau by uniting the oblongs left over from the regular coin work of the Bureau, which were of widely varying finenesses, and, without any special mixing, weighing up samples of 3.75 grams. Ten envelopes were sent to each one of the institutions and Table IX summarizes the results reported. As this sample had no claim to uniformity all the results reported are given:

TABLE IX—ASSAYS OF BUREAU COIN SCRAP SAMPLE

Fineness	Lab. No. 1	Lab. No. 2	Lab. No. 3	Lab. No. 4	Total
898.6		4			4
898.7					
898.8					
898.9		7	2		9
899.0	1				1
899.1		1	12	8	21
899.2	4				4
899.3		6	6		12
899.4	2				2
899.5	6	12	6	20	44
899.6	6				6
899.7	3				3
899.8	1		4		5
899.9					
900.0				2	2
Lost	4				4
Total.....	30	30	30	30	120

The laboratory numbers here are the same as in Table VIII.

As a final test of the method when practically applied to ingot work, three large samples were taken from each one of nine melts of ingots and assayed in various laboratories. Each sample was assayed in duplicate five times and in triplicate once, making a total of 39 determinations on each melt. Table X summarizes the results reported.

TABLE X—ASSAYS OF NINE COIN INGOT MELTS

Fineness	Melts									Total
	1	2	3	4	5	6	7	8	9	
897.7	1									1
898.0	1	1	1							3
898.2	1	2	1							4
898.4			1							1
898.6	7	5	7	3	1					23
898.7	1									1
898.8	3		3			1				7
898.9	7	1	3	1	3					15
899.0						2	2	1		5
899.1	12	4	10	15	10	7	2	3	5	68
899.2						2				2
899.3	1	4	4	6	7			2	8	32
899.4						2		5		7
899.5	5	8	8	13	14	15	16	19	17	115
899.6		2	1			4	3	5		15
899.7		3				3	3	1		10
899.8					1	1	4	1	1	8
900.0		7		1	3	1	5	2	8	27
900.1						1	4			5
900.4		2								2
Totals ..	39	39	39	39	39	39	39	39	39	351

As a general conclusion from the elaborate tests herein given, it may be stated that two operators, working upon identical samples of standard silver and making four determinations each, may differ as much as 1 fine in their reports. Having thus established the capacity of the method as at present carried on as a commercial operation, attention is now being given to improving the method so as to reduce the allowable limit of difference.

It may seem unnecessary to many of my readers, but my experience shows that there is much confusion and uncertainty in stating the composition of precious metal bullion. This is generally done in parts per thousand or fineness. It is similar to stating composition by percentage, but in bullion work there is much misunderstanding regarding the decimal point. Intelligent people who would never think of expressing fifty per cent. by ".50%" habitually write five hundred fine as ".500 fine" and incorrectly use the decimal point before the numerals in stating fineness. Whenever "fine" or "fineness" or an equivalent expression is used in stating the composition of bullion the decimal point should not be used unless the figures following it express a quantity less than 1 fine. Again, some people incorrectly use a preliminary "o" when the fineness is less than 100. They would not think of writing ".05 per cent." but habitually do write ".052 fine." Again, some people mistake fineness as being the exact equivalent of percentage, but it is only $\frac{1}{10}$ of percentage, and in considering the accuracy here shown by the Gay-Lussac method it should be noted that 1 fine is the equivalent of 0.1 per cent.

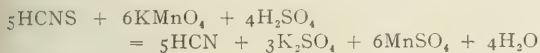
THE SULFOCYANATE-PERMANGANATE METHOD FOR COPPER IN ORES

By D. J. DEMOREST

Received November 12, 1912

Under the proper conditions copper may be precipitated practically completely as cuprous sulfocyanate. It is true that a qualitative test for copper may be obtained in the filtrate from the cuprous sulfocyanate when potassium ferrocyanide is added but this is due to the presence of only about 0.0001 gram of copper, as the writer has found by colorimetric measurements. Furthermore, the writer has found that practically all the copper added to the solution before precipitation may be recovered from the precipitate by electrolysis.

In Guess's method for copper the cuprous sulfocyanate is dissolved on the filter with sodium hydroxide, leaving the cuprous hydroxide on the filter while sodium sulfocyanate goes through. The filtrate is then made acid with sulfuric acid and is titrated with permanganate. Theoretically, the titration reaction is



Practically, however, the oxidation in acid solution is never complete and an empirical factor must be used amounting to about 5 per cent. of the copper present, according to Guess's tables of correction given in Low's "Technical Methods of Ore Analysis." This is also in accord with the writer's experience and with that of Grossman and Hölter.¹

It occurred to the writer that if the permanganate were added to the sulfocyanate in alkaline solution until about as much was added as would be required to titrate the sulfocyanate in acid solution and if then the solution were made acid, the titration might be finished by a few drops, and in this way complete oxidation might be brought about and no empirical factor would be needed.

It is easy to tell when enough permanganate has been added to the alkaline solution by testing a drop or so on a white plate with a drop of an acid solution of ferric chloride. If not enough permanganate has been added a red color develops but if enough has been added no red appears. It is not necessary to run in permanganate until no red is obtained on testing. When the red color of the test is very faint the solution may be made acid and the titration finished in the usual way.

PROCESS OF ANALYSIS

Weigh out enough of the ore to have from 0.05 gram to 0.30 gram of copper present. Transfer the sample to a 200 cc. beaker, add 5 cc. of strong hydrochloric acid and heat for several minutes; then add 20 cc. of nitric acid and digest on a hot plate until the ore is completely decomposed. Then add 10 cc. of 1 : 1 sulfuric acid and boil down until fumes of SO_3 appear. Cool and add 50 cc. of water containing 3 grams of tartaric acid and heat until all soluble salts are in solution. Cool and add ammonia until

the solution turns a deep blue, then add sulfuric acid until the liquid becomes acid, then add one cc. more. Now add one gram of sodium sulfite dissolved in 20 cc. of water, heat nearly to boiling and add slowly and with vigorous stirring one gram of potassium sulfocyanate dissolved in 20 cc. of water. Heat at a nearly boiling temperature for several minutes to coagulate the precipitate and dissolve out of it all tartaric acid. Cool somewhat and filter while still hot through, preferably, an asbestos mat on a Gooch filter. Wash well with water and rinse out the suction flask. Then pour through the crucible 30 cc. of a hot 10 per cent. sodium hydroxide solution and wash well with water.

Warm the filtrate to about 50° and proceed to titrate. Run in slowly at first, while the flask is vigorously shaken, the standard permanganate solution. The solution in the flask turns green, due to the K_2MnO_4 formed. After about 10 cc. have been run in take out a drop of the solution and place it in a drop of strong hydrochloric acid on a paraffined white plate; then add a drop of a 10 per cent. solution of ferric chloride. If a red color appears continue to add the permanganate solution, testing after each 5 cc. until the red becomes weak, then test more frequently until the red color of a test becomes quite faint. Then add 30 cc. of 1 : 1 sulfuric acid and shake the flask until the MnO_2 all dissolves and finish the titration to the usual permanganate end point. This will require perhaps one cc. of permanganate.

NOTES ON THE PROCESS

Fairly close results may be obtained by titrating carefully in the alkaline solution until five drops of the solution give no red color with ferric chloride. But it is easier and more accurate to titrate only to an approximate end in the alkaline solution and finish in an acid solution. It is important that the precipitation be made as above directed with vigorous stirring and that the solution be digested on the hot plate after precipitation.

Under the conditions of titration the permanganate is reduced in the alkaline solution thus: $2\text{KMnO}_4 = \text{K}_2\text{MnO}_4 + \text{MnO}_2 + 2\text{O}$. The oxygen possibly oxidizes the sulfocyanate to tetrathionate, but of this the writer is not sure. He has proved by filtering off the MnO_2 and weighing it and by titrating the manganate in the filtrate that the permanganate is reduced as above written. However, it makes no difference what reaction takes place in the oxidation of the sulfur in the alkaline solution, since the test for sulfocyanic acid is made on the plate in a strongly acid solution and the reaction between the sulfocyanate and the manganate and manganese dioxide completes itself there. The manganese dioxide does not settle out of the solution unless it stands a long time.

According to the titration reaction given in the second paragraph of this article 5 atoms of copper are equivalent to 6 molecules of KMnO_4 or 30 atoms of iron. Therefore, the iron value of the permanganate multiplied by $\text{Cu}/6\text{Fe}$ or 0.1897 gives the copper value of the permanganate. The permanganate used

¹ Grossman and Hölter, *Chem. Ztg.*, **33**, 348.

by the writer equals 0.01 gram Fe, or 0.001897 gram Cu per cc.

After the filtrate has cooled, a crystalline compound of tartaric acid may separate. Hence the solution should be filtered hot.

The following are some results obtained by the above method:

COPPER		COPPER	
Present	Found	Present	Found
0.1870	0.1890	0.0600	0.0596
0.1503	0.1511	0.0605	0.0603
0.1117	0.1125	0.1610	0.1630
0.1666	0.1668	0.0663	0.0667
0.0940	0.0930	0.1103	0.1109
0.2005	0.2017	0.1140	0.1147
0.2220	0.2224	0.1000	0.1001
0.2220	0.2210	0.1000	0.0999

The later results were the most accurate and were obtained after the necessity of digesting the precipitate in the hot solution was learned.

No elements interfere except, according to Low, silver. This is easily removed. If there is any lead present, the lead sulfate obtained after evaporating to fumes of SO_3 should be filtered off after the soluble salts are dissolved.

DEPARTMENT OF METALLURGY
OHIO STATE UNIVERSITY
COLUMBUS

ELECTROLYTIC DETERMINATION OF COPPER IN ORES, CONTAINING ARSENIC, ANTIMONY OR BISMUTH

By D. J. DEMOREST

Received November 1, 1912

Ores containing arsenic, antimony or bismuth have been best analyzed for copper by the iodide method, for the copper must be separated from these elements before it can be accurately determined electrolytically. To separate the copper from these interfering elements, by the old method of precipitating the sulfides, dissolving the arsenic and antimony sulfides in sodium sulfide and then the copper sulfide in potassium cyanide is tedious and troublesome. The following method greatly reduces the time required and gives very accurate results.

It has long been known that under the proper circumstances copper can be precipitated free from arsenic, antimony or bismuth as CuCNS . Guess's permanganate method is based upon this precipitation. However, owing to the solubility of the CuCNS as ordinarily precipitated, a considerable correction factor was necessary.

While working on the analysis of Babbitt metals high in antimony and tin, the writer observed that the copper was apparently entirely precipitated as CuCNS from a solution containing ammonium sulfate, ammonium tartrate and tartaric acid. When the method was applied to the analysis of impure ores, it proved successful. It is as follows:

One gram, or more if the sample is low in copper, is treated with 7 cc. of HCl and 7 cc. of HNO_3 . The solution is heated until the ore is decomposed, then 5 cc. of sulfuric acid are added and the liquid evaporated to copious fumes of sulfuric acid. Now 30 cc. of water containing 3 grams of tartaric acid are added, and the

solution is heated until all soluble salts are dissolved; then it is cooled somewhat and ammonia is added until alkalinity is reached. Now H_2SO_4 is added until the solution becomes acid, and then one cc. more. To the solution, which will now be hot, is added 2 grams of sodium sulfite, and the solution is stirred until it is all dissolved. Then 1 gram of KCNS dissolved in a few cc. of water is poured in. The copper precipitates immediately as CuCNS . The solution is stirred vigorously and heated to boiling; then the precipitate is allowed to settle for a few minutes. The precipitate is very dense. The solution is filtered through a dense filter and washed several times with a solution containing about 1 per cent. of KCNS and the same amount of tartaric acid.

Onto the filter paper, which should be held in a rather large funnel, is poured 18 cc. of 1 : 2 nitric acid and the funnel is immediately covered with a watch glass to prevent loss by spraying, due to the vigorous action of the nitric acid on the CuCNS . When the acid has run through, the filtrate is heated to boiling and poured through again; the paper, funnel and watch glass are washed well with water, care being taken to keep the volume of the filtrate as small as possible. The solution is now heated to vigorous boiling for five minutes to destroy the HCNS , water is added to make the volume about 125 cc., and the copper is precipitated by electrolysis, using a gauze cathode, a drop of potential of three volts and a current of three amperes. Precipitation should be complete in from thirty minutes to an hour. The copper should precipitate in a beautiful and crystalline condition. If it does not the solution was not boiled long enough.

If the ore contains lead, some will precipitate when the sodium sulfite is added, but this does no harm. The tartaric acid prevents the precipitation of antimonious acid.

The sulfoeyanic acid must be completely destroyed before electrolysis or the copper will come down in a spongy and non-adherent form. Instead of dissolving the CuCNS in nitric acid, the precipitate and filter paper may be ignited in a porcelain crucible until all carbon is burned off and the CuO dissolved in 5 cc. of nitric acid, diluted and electrolyzed.

The following are some results obtained with the method:

Copper	GRAMS OF METALS PRESENT					GRAMS COPPER FOUND
	Arsenic	Antimony	Bismuth	Iron	Lead	
0.1000	0.07	0.07	0.100	0.100	0.100	0.0997
0.1000	0.07	0.07	0.100	0.100	0.100	0.0999
0.1000	0.07	0.07	0.100	0.100	0.100	0.0995
0.1000	0.07	0.07	0.100	0.100	0.100	0.1000
0.1500	0.07	0.07	0.100	0.100	0.100	0.1495
0.1500	0.07	0.07	0.100	0.100	0.100	0.1495
0.1500	0.07	0.07	0.100	0.100	0.100	0.1500
0.1500	0.07	0.07	0.100	0.100	0.100	0.1500
0.1500	0.07	0.07	0.100	0.100	0.100	0.1499

It is the writer's belief that this is the most accurate and usable electrolytic method for copper on ores containing arsenic, antimony or bismuth.

DEPARTMENT OF METALLURGY
OHIO STATE UNIVERSITY
COLUMBUS

AN ELECTROLYTIC METHOD FOR THE DETERMINATION OF TIN IN CANNED FOOD PRODUCTS

By ALLERTON S. CUSHMAN AND EVERETT B. WETTINGER

Received November 18, 1912

The issuance by the United States Department of Agriculture under date of September 30, 1910, of Food Inspection Decision, No. 126, governing salts of tin in food, which allows no more than 300 mg. of tin to the kilogram of material, has been the occasion of a number of laboratories being called upon to make a special study of the subject. These investigations have necessitated thousands of determinations of tin in every conceivable form of canned food. The usual analytical method for estimating very small quantities of tin contained in foods is difficult, tedious, and requires the evaporation of from 150 to 200 cc. of strong acids. When a considerable number of determinations have to be made, the question of a hood and draft, which will take care of such large quantities of acid fumes, presents a very difficult problem.

The gravimetric method as used in the laboratories of this Institute is briefly as follows: The entire contents of a can is pulped by maceration in a large porcelain mortar: 50 grams of the sample are transferred to a 9-inch evaporating dish. From 50–150 cc. of strong nitric, and from 20–50 cc. strong sulfuric acid are added, according to the nature of the sample. (Beets, spinach, asparagus, etc., require less acid than beans, sweet potatoes, corn, or fruit, to which a large amount of sugar has been added.) The mixture in the evaporating dish is covered with a watch glass and heated over a strong Bunsen flame until sulfuric acid fumes begin to come off. Nitric acid is added repeatedly until the solution is colorless. The solution is diluted with a large volume of water and neutralized with strong ammonium hydroxide, making a total volume of 300–500 cc. The solution is made slightly acid with HCl, transferred to a flask

of yellow ammonium sulfide and reprecipitated with glacial acetic acid. The tin sulfide together with some precipitated sulfur is filtered on a weighed gooch, dried in a water oven, ignited over a Méker burner, and weighed as stannic oxide, SnO_2 . Factor for metallic tin, 0.7882.

If occasion requires, a single determination can be rushed through by the above method in one working

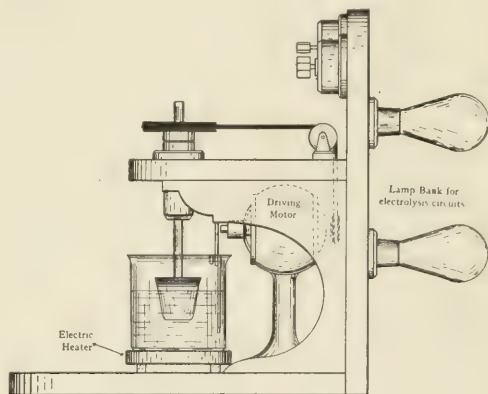


FIG. 2—SIDE ELEVATION

day, but in the usual routine in which the samples are worked in batches, from two to three days are consumed in getting out results. The hoods and flues suffer great damage from the acid fumes and the cost of the acids consumed in total destruction of the organic matter is very high.

These objections to the current method of analysis led us to investigate all possible ways of shortening and improving the method, with the principal object in view of avoiding the destruction of the organic matter by long digestion in nitro-sulfuric acid. In the preliminary experiments, the expedient was tried of cooking the slightly acid sample in an aluminum pan with the object of separating the tin from the organic matter preliminary to its re-solution in stronger acid and preparation for separation by electrolysis. It was believed that this method would aid in the separation of tin from the organic colloids in which it was held, but subsequent experiment showed that the preliminary cooking in an aluminum utensil was unnecessary and the simple method as finally worked out is as follows: 50 grams of the pulped material are placed in a 600 cc. beaker and brought to a slow boil with 50 cc. of concentrated hydrochloric and 25 cc. of nitric acid. The mixture is stirred continuously and the boiling continued five minutes unless there is danger of foaming, in which case the flame is removed and the material allowed to digest for ten minutes. The solution is then diluted with about an equal quantity of water, made alkaline with strong ammonia and 25 cc. of saturated ammonium sulfide. The mixture is digested for a few minutes with thorough stirring, and all insoluble organic matter filtered out on a ribbed filter. The washing is done with boiling water containing a little ammonium sulfide. About 150 cc. of wash water are used in five separate washings,

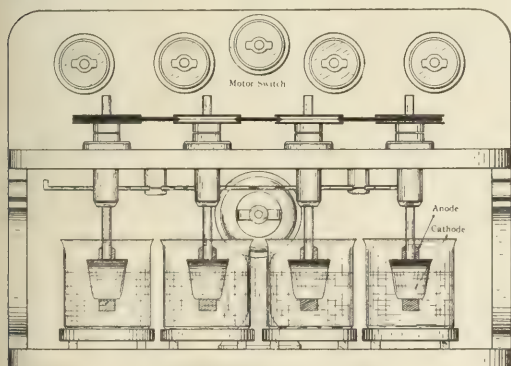


FIG. 1—FRONT ELEVATION

and a slow stream of H_2S passed through it for two hours. The flask is heated on the water bath for an hour or allowed to stand over night to settle the tin sulfide. The solution is then filtered and the precipitate washed alternately with a solution of ammonium acetate and water. The tin sulfide is dissolved through the filter with three successive portions

making the total solution to 400 cc. The solution is then electrolyzed hot, using 1.5 amperes at 6 volts. A rotating cathode is used. The end of the revolving spindle carries a rubber stopper over which a clean weighed platinum crucible is slipped. The apparatus which has been found convenient for carrying out the electrolysis of a number of determinations at the same time is shown in front elevation in Fig. 1 and in side elevation in Fig. 2. From one to four hours is necessary to complete an electrolytic run, two hours being generally sufficient, except in cases in which the tin content is very high. At the end of a run the crucibles are cleaned by heating in a solution made by mixing 100 cc. of 10 per cent. oxalic acid with 100 cc. of concentrated nitric acid.

Numerous experiments were made with the electrolytic apparatus which showed that tin could be recovered with a fair degree of accuracy from an ammonium sulfide solution. Some of these results are given in Table I.

TABLE I

Sample No.	Tin added mg.	Tin found mg.	Time taken
1.....	1.0	1.1	1 hour
2.....	1.0	1.0	1 hour
3.....	10.0	9.8	2 1/4 hours
4.....	10.0	9.9	2 1/4 hours
5.....	10.0	10.0	2 1/3 hours
6.....	10.0	10.0	2 1/3 hours
7.....	25.0	24.6	2 3/4 hours
8.....	50.0	50.5	4 hours

The next step was to study the effect of organic food material on the method. Tomatoes were put into glass bottles with 50 cc. of a ten per cent. sodium chloride solution, and 10 mg. of tin in solution were then added to each bottle. The bottles were corked and autoclaved under pressure in a manner similar to the processing of canned foods. The results of analysis are given in Table II.

TABLE II

No.	Tin added mg.	Tin recovered mg.	Time of electrolysis
1.....	10	9.9	2 hours
2.....	10	9.2	2 hours
3.....	10	10.1	2 hours
4.....	10	9.9	2 hours

In run No. 2 the cork blew out of the bottle during

TABLE III

MATERIAL	Tin found Mg. per kilo		Time, hours
	Run I	Run II	
Apple butter A.....	178	180	3
Apple butter B.....	142	142	2.5
Apple butter A.....	168	168	2.5
Apple butter B.....	142	142	2.5
Blackberries.....	28	26	2.5
Rhubarb A.....	170	174	2.5
String beans.....	72	64	2.5
Beef soup(a) (solid).....	18	22	2.5
Tomato soup.....	74	74	2.5
Bouillon soup.....	28	26	2.5
Oxtail soup (solid).....	66	76	2.5
Vegetable soup (solid).....	22	36	2.5
Mock turtle soup (solid).....	20	20	2.5
Baked beans with tomato sauce.....	40	42	2.5
Baked beans without tomato sauce.....	8	10	2.5

(a) All the soups except the bouillon and tomato were solid and contained large amounts of meat and vegetables.

processing and it was known that a slight amount of the contents had been lost. These results were very

encouraging as the determination of small amounts of tin in the presence of an excess of organic food material must be but a fair approximation of the truth at the best. The next step was to try the method on a large variety of food products. The results of a number of duplicate runs are given in Table III.

The results given in Table III show that it is possible to produce satisfactory check results when working in duplicate by the method, and, in fact, the checks are generally much closer than can be expected when working with the longer gravimetric method. In each analysis the insoluble residue, consisting of food pulp, was carefully examined for tin, but if any was present it was in such small amount that it could not be found by qualitative tests.

In Table IV the results are given of a series of analyses of various foods when the gravimetric and electrolytic methods were both used.

TABLE IV

MATERIAL	Tin found Mg. per kilo	
	Electrolytic method	Gravimetric method
Tomato soup.....	145	130
Rhubarb.....	112	102
Squash.....	316	314
Spinach.....	35	22
String beans (liquid portion).....	94	70
String beans (solid portion).....	340	356
String beans (total).....	229	226
Beets (solid portion).....	70	27(a)
Cuthbert raspberries.....	248	222
Sweet potatoes.....	40	39
Pork and beans.....	64	73
Sauer-kraut.....	12	13
Apple-butter.....	142	112
Blackberries.....	27	17

(a) Result probably low.

An inspection of Table IV shows a generally satisfactory agreement between the results obtained by the two methods, and it should be stated that these are not selected results but are given directly in the order in which they were obtained by two different workmen. Only about three hours are required to get out a series of results by the electrolytic method, the number in the batch being limited only by the number of electrolytic cells available in the laboratory. With the gravimetric method usually the best part of three days is required to produce a batch of determinations, the number being in this case limited by the hood and flue space available. In the saving of time, acids and other reagents consumed and in destruction to flues and the laboratory generally, the advantage is all on the side of the electrolytic method. If considerable work of this kind has to be done, the first cost of the electrolytic apparatus is fully justified.

THE INSTITUTE OF INDUSTRIAL RESEARCH
WASHINGTON, D. C.

POTASSIUM PERMANGANATE IN THE QUANTITATIVE ESTIMATION OF SOME ORGANIC COMPOUNDS¹

By C. M. PENCE

Potassium permanganate has been most generally used in the volumetric estimation of iron. Some uncertainties formerly existed since it was impossible to obtain a chemically pure article and insufficient data were

¹ Read before the Indiana Section of the American Chemical Society, May 10, 1912.

at hand as to proper methods of preparation and standardization of its solutions.

At present, these objections have been largely overcome and almost all of our text-books on quantitative analysis contain an extended treatise on proper means of preparation and standardization of volumetric permanganate solutions.

One of the most commonly known organic compounds that is quantitatively determined by the use of volumetric permanganate is oxalic acid. Now oxalic acid and iron are determined in acid solution, but the procedure most applicable for the oxidation of all types of aromatic compounds as well as carbohydrates and hydrocarbons is with alkaline permanganate. Oxidations in acid solution are less energetic than those with alkaline KMnO_4 and in the latter case the final product of a completed decomposition of the organic compound is oxalic acid instead of CO_2 and H_2O .

Among the substances mentioned in the literature¹ as being oxidized to oxalic acid are propylene, isobutylene, amylene, acetone, fatty acids; butyric, lactic, succinic, and tartaric acids; dextrose, sucrose, glycerol and phenol. Now when an organic compound is oxidized to oxalic acid, a further oxidation to CO_2 and H_2O readily follows upon acidifying and warming the solution. Such a procedure forms the nucleus of a method for the determination of the compounds previously enumerated. Tocher made use of this method and found that phenol could be determined. His method was substantially as follows: Dissolve 1 gram phenol in 1000 cc. distilled water and take 10 cc. for titration. Add 3-4 grams NaHCO_3 together with a little distilled water. Then add 50 cc. KMnO_4 and boil for five minutes. Set aside to cool and gradually add dilute H_2SO_4 to decided excess; warm to 60°C . and titrate the excess of $N/10$ KMnO_4 with $N/10$ oxalic acid.

This method was found to be open to the following objection: that the manganese dioxide formed as a result of the action of $N/10$ KMnO_4 upon the phenol did not reduce readily enough with consequent solution upon direct titration with $N/10$ oxalic acid. Thus the solution was full of oxide which not only obscured but rendered the end point of little value, in that the oxide was not completely reduced before the permanganate end point was obtained.

The following modification of Tocher's method was found to give good results:

Dissolve 0.4 gram phenol in 1000 cc. distilled water. Place 50 cc. $N/10$ KMnO_4 and 3 to 4 grams NaHCO_3 in a 500 cc. glass-stoppered Erlenmeyer flask. Add 25 cc. of the phenol solution with gentle rotation. Boil 5-10 minutes (with stopper removed). Cool flask to about 60°C . Acidify with dilute H_2SO_4 , let stand about 2 minutes; cool to room temperature.

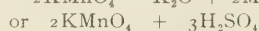
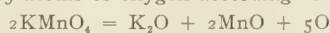
¹ "Oxidation of Organic Compounds with Alkaline Permanganate," Eduard Donath and Hugo Ditz, *J. prakt. Chem.*, [2] **60**, 566-576 (1899); through *J. Chem. Soc.*, [1] **78**, 197 (1900). "Contribution to the Knowledge and Determination of the Carbohydrates," J. König, W. Greifenhagen and A. Scholl, *Z. Nahr. Genussm.*, **22**, 705-723; through *Abstr. J. Am. Chem. Soc.*, **6**, 901 (1912). "Volumetric Determination of Phenol," Jas. F. Tocher, *Pharm. J.*, **66**, 360.

Dilute with distilled water, add 5 cc. 20 per cent. KI and titrate the liberated iodine with $N/10$ thio-sulfate solution, using starch as indicator. The number of cc. of $N/10$ thiosulfate subtracted from the number of cc. KMnO_4 originally added = no. cc. of KMnO_4 consumed by the phenol.

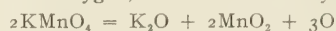
1 cc. $N/10$ KMnO_4 = 0.000336 gram phenol.

If a glass-stoppered Erlenmeyer flask is not available an ordinary Erlenmeyer may be used and its contents transferred to a glass-stoppered bottle before acidifying. Any oxide adhering to the Erlenmeyer is easily removed by the addition of a little distilled water acidified with H_2SO_4 and containing a few drops of 20 per cent. KI.

In considering the nature of the oxidation with KMnO_4 in acid and alkaline solutions it is observed that each molecule of KMnO_4 in acid solution liberates 2.5 atoms of oxygen according to following equation:



Now in alkaline solutions the two molecules of MnO are immediately oxidized to 2 MnO_2 at the expense of 2 atoms of oxygen, so that we actually have



Hence, for each molecule of KMnO_4 used, only $1\frac{1}{2}$ atoms of oxygen are available for our oxidation process. This fact must be recognized in providing sufficient KMnO_4 to readily complete the oxidation process, and it would necessarily enter into a calculation of the value of $N/10$ KMnO_4 in terms of phenol if the MnO_2 , or rather its hydrated form, were filtered from the solution before acidifying and adding the KI. But since the procedure is not lengthened by a filtration the MnO_2 is reduced to its manganous form with the liberation of free iodine, and we must calculate our factor by considering that reaction proceeds as in acid solution with 2.5 atoms of oxygen available per molecule of KMnO_4 , although such is not literally the truth.

To completely oxidize phenol, 14 atoms of oxygen are required, according to the following equation:



Since only 2.5 atoms of oxygen are available per molecule of KMnO_4 , then 5.6 molecules of KMnO_4 would be required for every molecule of phenol and the factor for $N/10$ KMnO_4 in terms of phenol becomes:

Mol. wt. phenol

$$2.5 \times 2 \times 10 \times 5.6 \times 1000$$

Experiments with a phenol solution containing 0.0005 gram of phenol, per cc. as determined by the Koppeschaar bromine method, resulted as follows:

Exp. No.	Grams phenol taken	Per cent. phenol found
1.....	0.0050	99.65
2.....	0.0050	100.18
3.....	0.0075	99.65
4.....	0.0076	99.86
5.....	0.0100	99.86
6.....	0.0100	99.72

Now when the cresols were run in the same manner as phenol it was found that they were not completely

oxidized and that they varied slightly as to the rate with which oxidation proceeded; hence, any permanganate method for their accurate determination must depend upon definitely fixed conditions.

Likewise, it was obvious that commercial creosote and guaiacol could not be determined by this procedure, since they are mixtures of several more or less related phenols that are not present in like proportion in different specimens. However, with single solutions of several common phenols and closely related compounds, fairly gratifying results were obtained. Pyrogallol, pyrocatechin, resorcinol and hydroquinone, from all of which the CH_3 group is absent, were readily and completely oxidized.

Benzoic acid was very slightly attacked while under similar conditions salicylic acid and salol were completely oxidized. Thus it would seem that the phenolic OH group predisposes towards a complete oxidation and that many uninvestigated phenols and closely related compounds would give analogous reactions. In making up solutions of the several phenols, sufficient $\text{N}/2$ NaOH was added when necessary, to insure ready solution.

The following table is self-explanatory:

SUBSTANCE	PER-CENTAGE FOUND	SUBSTANCE	PER-CENTAGE FOUND
Pyrogallol	{ 100.4	Hydroquinone.....	{ 99.49
	{ 100.1		{ 99.56
Pyrocatechin..	{ 100.2	Salicylic acid.....	{ 99.79
	{ 99.9		{ 100.2
Resorcinol.....	{ 100.5	Salol.....	{ 99.77
	{ 100.4		{ 99.91

The alkaline permanganate method is especially applicable for the quantitative estimation of the above compounds when they occur individually in very small amounts in single solutions or in conjunction with substances not readily oxidized.

DEPARTMENT OF CHEMICAL RESEARCH
ELI LILLY & CO., INDIANAPOLIS

SOME PROPERTIES OF KOJI-DIASTASE

By G. KITA

Received September 18, 1912

The properties of the saccharifying enzymes of koji (a culture of *aspergillus oryzae* on steamed rice) have been studied by many investigators and are supposed to be comparatively well understood. There are, however, certain obscurities which exist in regard to the identification and classification of these enzymes. They must be cleared up on account of their scientific and practical importance.

I have lately been occupied in a series of investigations relative to Soya or Shoyu (Japanese sauce fermented from beans, wheat and salt) making, and incidentally cleared up certain of the above points.

1. IS SACCHARIFICATION OF STARCH BY KOJI-DIASTASE CARRIED OUT BY TWO DIFFERENT ENZYMES, DIASTASE (AMYLASE) AND GLUCASE, SUCCESSIVELY?

It has been generally thought that koji contains two kinds of saccharifying enzymes, *viz.*, diastase (amylase) and glucase, and it is supposed that the glucose present in a liquid saccharified by means of

koji is produced by the two enzymes above mentioned. It has been affirmed by some investigators that while the glucase present in koji does not act rapidly, yet, the sugar finally produced in the saccharification of starchy matters with koji is invariably glucose, and that maltose is present only in a negligible quantity. Evidence in support of the above assertions is still meager and I was led to think that there may be present in koji another new enzyme, which is altogether different from glucase, and which can convert starch directly to glucose without intermediate steps. The following experiments were made:

Experiment 1.—To each 200 cc. of a 2 per cent. solution of maltose (moisture = 4.25 per cent.) and also starch (moisture = 16.99 per cent.), 20 cc. of the solution of enzymes (corresponding to 2 grams of koji) were added. After allowing the enzymes to act for three hours at 50° C., the reducing action of the digested liquid on Fehling's solution was tested and a rough estimation of glucose was made by means of the glucosazone reaction.

In the determination of the osazone, 100 cc. of each liquid were boiled 1½ hours with 4 grams of phenylhydrazine hydrochloride and 6 grams of sodium acetate, filtered and washed with 100 cc. boiling water. This, of course, cannot be said to be a perfect method either for the isolation or determination of glucosazone, but is sufficiently accurate for comparison of results.

Solution acted upon by enzymes	Starch	Maltose
Cc. saccharified solution required to reduce 50 cc. Fehling's solution.....	18.6	21.0
Grams of glucosazone obtained from 100 cc. of saccharified solution.....	0.2575	0.1164

Experiment 2.—A like experiment was performed with Taka-diastrase. In this case each 100 cc. of a 2 per cent. solution of maltose and starch, respectively, was hydrolyzed with 20 cc. of a 1 per cent. solution of the enzyme. For the determination of glucosazone 50 cc. of each solution were taken:

Kind of solution acted upon by enzymes	Starch	Maltose
Cc. saccharified solution required to reduce 50 cc. Fehling's solution.....	30.0	23.6
Grams of glucosazone obtained from 100 cc. of saccharified solution.....	0.2088	0.0772

As will be seen in the above experiment, the reducing power of the starch solution after digestion is so strong that we can hardly compare the rate of hydrolysis of maltose to that of starch. Moreover, the quantity of glucosazone from the starch solution is very much higher. The presence of dextrine in the production of glucosazone does not seem to possess remarkable influence, but the presence of maltose has a tendency to give an increased quantity of glucosazone when phenylhydrazine hydrochloride is used in excess. Therefore, in the hydrolysis of starch by means of koji-diastrase, it is evident that glucose is not produced principally by the action of glucase, but directly without the aid of it. Dr. Nishisaki¹ asserts that in the case of saccharifying starch by means of koji, the sugar produced thereby is composed in its first stage, of maltose, on account of the weak activity

¹ J. Chem. Soc., Tokyo, 29, 325.

of glucase. But this must have arisen from an error because of his presumption of the presence of malt-diastase in koji.

II. INFLUENCE OF SALT ON ENZYMES IN KOJI

It is a well-known fact that enzymic activity is lost by heating, but so far as I know the effect of heating it in the presence of salt has not yet been investigated. In the soya mash, enzymes act in salt solution and it is, therefore, necessary to find out the relation of enzymes toward heat in the presence of salt. With this object in view, I made the following experiments which have fortunately proved that NaCl has a protecting influence on koji-diastase but not on malt-diastase; while Na_2HPO_4 , asparagin, and H_2SO_4 have an injurious effect even on koji-diastase.

Experiment 3.—One hundred cc. of a 2 per cent. starch solution, taken in each of three different vessels, were digested for two hours at 50°C . with 5 cc. solution of enzymes (100 grams koji or malt macerated in 1,000 cc. water for 10 hours), into two of which 20 grams of NaCl were added in two ways: one from the beginning and the other after digesting for three hours. The remaining one was kept blank for control.

NO. OF CC. OF THE SACCHARIFIED SOLUTION USED FOR THE REDUCTION OF 50 CC. FEHLING'S SOLUTION

No.	Kind of digestion	Enzymic solution from koji	Dried malt	Green malt
1	Not heated.....	50.2	41.4	25.2
2	Heated 3 hrs. at 50°C . and added NaCl..	67.6	90.0	25.2
3	Heated 3 hrs. at 50°C . after addition of NaCl.....	55.6	200.0	57.4

Experiment 4.—The experiment was carried as in Experiment 3, except that Na_2HPO_4 , asparagine and H_2SO_4 were used instead of NaCl. For 100 cc. koji extract, 5 grams Na_2HPO_4 , 5 grams asparagine or 14 cc. of 1 per cent. H_2SO_4 solution were added.

NO. OF CC. OF THE SACCHARIFIED SOLUTION USED FOR THE REDUCTION OF 50 CC. FEHLING'S SOLUTION

No.	Kind of digestion	Enzymic solution with asparagine	Na_2HPO_4	H_2SO_4
1	Not heated.....	35.2	57.0	87.5
2	Heated before addition.....	44.5	65.4	100.0
3	Heated after addition.....	92.5	112.4	140.0

III. THE INFLUENCE OF SALT ON SACCHARIFYING ACTIVITY OF KOJI-DIASTASE

The results obtained by previous investigators with regard to the influence of salt, acid, etc., on the saccharification by malt- and koji-diastase agree on the point that a very small quantity of these substances acts favorably, but that increase of the same is injurious.

Among various authors, Dr. Saito¹ says that the activity of koji-diastase is injured by the presence of salt, for instance, in a ten per cent. salt solution its activity is lessened to 11.3% and in twenty per cent. solution to 7.6 per cent. S. Mori,² however, says that a large quantity of NaCl gives no inhibitory influence on koji, but he attributed this observed influence to a peculiarity of some kinds of koji. His result is inaccurate since a development of organisms took

place in his experiment. At that time, I¹ also observed the similar curious phenomenon which led me at once to entertain an opinion like Mori. Men employed in soya-making alleged that in practice where a considerable quantity of salt is present in mash, no retarding of enzymic action is noticed. Such diversity of opinion was found lately to have originated in the fact that when the enzymic solution is concentrated a large quantity of sodium chloride does not apparently exert an inhibitory influence, while in a less concentrated enzymic solution even a smaller quantity of salt will have a very injurious action. In general, the influence of salt on diastase is related to the concentration of the enzym solution. The following experiments show this relation clearly:

Experiment 5.—One hundred cc. of a 20 per cent. soluble starch solution with or without 40 grams NaCl were saccharified with 100 cc. koji extract (200 grams wheat koji extracted in 1000 cc. water) and were filtered after 16 hours standing at 50°C . The iodine reaction of the solution without salt was purple or light red after 10 or 30 min., respectively, while that of the salt-containing solution was somewhat deeper in color. After 30 min. 5 cc. concentrated caustic alkali solution were added in order to inhibit further diastatic action and then sugar was determined after diluting the solutions to five times their own volume. To the digestion which did not contain NaCl the same amount of NaCl was added as was in the other, so that the conditions might be similar in conducting the sugar determinations.

NO. CC. OF THE DILUTED SUGAR SOLUTION TO REDUCE 25 CC. FEHLING'S SOLUTION

Digestion with NaCl	Digestion without NaCl
16.5	15.0

Experiment 6.—One hundred cc. of a 2 per cent. or 20 per cent. soluble starch solution were saccharified with 10 cc. of the koji extract at 50°C . wherein 20 grams NaCl were added before or after digestion. After the digestion was over, NaCl was added to the one which did not contain the same, as was done in the previous experiment.

The reaction of iodine toward these liquids was tested and the following result was obtained:

Duration of digestion in minutes	2 per cent. starch solution		20 per cent. starch solution	
	Digestion with NaCl	Digestion without NaCl	Digestion with NaCl	Digestion without NaCl
20	purple	red	blue	blue
30	red	red	blue	blue
60			purple	purple
120			red	red

Similar digestion was repeated after 30 minutes; 5 cc. caustic alkali solution were added in one case, and in the other after 120 minutes, so that further diastatic action is entirely arrested. Then, diluting the digestion in case of 30 minutes duration to five times and in case of 120 minutes duration to ten times its original volume, it was tested how many cc. of such dilution can completely reduce 25 cc. of Fehling's solution.

¹ *Centrbl. Bakt., II Abt.*, **17**, 102.

² *J. Pharm. Soc., Tokyo*, **311**, 1-10.

¹ *J. Chem. Soc., Tokyo*, **13**, No. 145, pp. 221-235.

No. cc. of the digestion to reduce 25 cc. Fehling's solution		120 minutes digestion	
30 minutes digestion			
with NaCl	without NaCl	with NaCl	without NaCl
23.2	17.8	48.8	30.3

Experiment 7. Two grams soluble starch in 500 cc. water with different quantities of NaCl were saccharified with 10 cc. koji extract at 50° C. After 30 min., 10 cc. alkali solution and NaCl were added so that each solution contained 100 grams NaCl in total solution.

REACTIONS TOWARD IODINE

No. of solution	No. of grams of NaCl added before reaction	After 10 min.	After 30 min.
1	0	red	red
2	20	purple	red
3	100	purple	purple

No. of solution	No. cc. of sugar solution to reduce 5 cc. Fehling's solution
1	17.0
2	26.0
3	45.0

In Nos. 5 and 6 we see that the influence of NaCl depends upon the concentration and not on the ratio of starch to the enzymic quantity. The more dilute is an enzymic solution the stronger is the inhibitory action of sodium chloride.

From Exps. 6 and 7 it is clear that the inhibitory action of NaCl does not relate to dilution when the proportion of NaCl to enzym is constant.

IV. CAN KOJI-DIASTASE BE PRESERVED IN BRINE?

The stability of the koji-diastrase in brine is not yet well known and it is a very important factor in soya making, where a long period of activity is necessarily maintained. I have kept diastase in brine for a month in summer and compared it with that kept in a dried condition in a desiccator. The result was as follows:

Experiment 8.—One hundred cc. of a 2 per cent. starch solution was saccharified for 3.5 hours at 50° C. with an enzymic solution (1 gram Taka-diastrase, 15 grams NaCl in 100 cc. water), and its reducing power was determined.

No.	Preservation of Diastase	No. cc. of saccharified solution to reduce 25 cc. Fehling's solution
1	In brine.....	30.8
2	In dry condition with envelope of black glazed paper.....	28.3
3	In dry condition in thin layer exposed to sunlight.....	33.4

It will be seen from these results that the diastatic power of the enzym in brine was stronger than that which was exposed to sunlight. The gelatine liquifying power of the same diastase was in the same order. From this and other data I have, I believe the strong diastatic power exerted in the old mash which was kept about a year was principally due to the koji originally used.

SUMMARY

I. Though koji may contain two different saccharifying enzymes, *viz.*, amylase and glucase, the total quantity of the glucose in a saccharified solution could not be produced from maltose by the action of glucase alone; hence, koji must contain some

other kind of diastase which produces glucose directly from starch without the aid of glucase.

II. Common salt has a protecting action on koji-diastrase under heating but not on malt-diastrase, while Na_2HPO_4 , asparagine and H_2SO_4 impair its activity more quickly.

III. The inhibitory action of salt on koji-diastrase has a certain relation to the concentration of diastase. In a dilute enzymic solution it is very strong but not in a concentrated enzymic solution. It is therefore necessary in every case to note concentration of diastase when we consider the influence of some salt upon it.

IV. The activity of koji-diastrase is conserved in brine for a long period.

DEPARTMENT APPLIED CHEMISTRY
TOKYO IMPERIAL UNIVERSITY

APPLICATION OF THE AMMONIUM CARBONATE METHOD FOR THE DETERMINATION OF HUMUS TO HAWAIIAN SOILS¹

By J. B. RATHER

Received November 12, 1912

The ammonium carbonate method for the determination of humus in soils² has been used on a number of samples of Texas soils, of different types met with in the United States, including the Travis, Orangeburg Houston, Laredo, Norfolk, Lufkin and Cameron series, and in every case the results have been entirely satisfactory, the "ash" averaging less than 0.40 per cent. While this method has proved to be reliable in this laboratory, it has been shown by Kelley and McGeorge³ that on certain soils of Hawaii the method does not give good results. This is due to the nature of the clay and not to the amount of clay present, for we have precipitated the clay completely in a solution containing 33.45 per cent. "ash" as determined by the official method.

Kelley and McGeorge modified the ammonium carbonate method by adding 4 grams ammonium carbonate per hundred cubic centimeters instead of 0.5 gram. This coagulated the clay in most cases, but they claim that the organic matter was partially precipitated.

These investigators propose a method for the removal of the clay by filtration by means of reduced pressure through a Pasteur-Chamberland tube and washing with ammonia as was done by Alway, *et al.*⁴ In connection with this it might be of interest to state that the filtration of humus solutions by reduced pressure has been done by Fraps and Hamner,⁵ who themselves do not claim originality for the process. Fraps and Hamner state that the method is very tedious and that organic matter may not pass through the filter. Neither Cameron, who first used the porcelain tube, Fraps and Hamner, nor Alway, *et al.*, recommended the method.

¹ Under the general direction of G. S. Fraps, chemist. Read at the meeting of the Association of Official Agricultural Chemists, Washington, D. C., September, 1912.

² THIS JOURNAL, 3, 660.

³ *Ibid.*, 4, 9, 604.

⁴ Nebraska Exp. Sta., *Bull.* 115.

⁵ Texas Exp. Sta., *Bull.* 129.

Although the types of soil such as are found in Hawaii may not occur in this country, on account of the simplicity and convenience of the ammonium carbonate method it was thought desirable to secure such a modification as would include such soils.

The soils used in this study were Hawaiian soils kindly furnished by Mr. McGeorge. After a number of trials to ascertain the most suitable conditions, the following method was adopted:

Prepare the solution as described in the official method, but decant the solution instead of filtering. Place 100 cc. in a graduated flask, add 2 grams ammonium carbonate, and heat on the steam bath for one hour. Allow to stand over night, pipette off 50 cc. of the supernatant solution, and evaporate to dryness in a tared dish. Dry three hours at 100° C., weigh, ignite, and weigh again. The loss in weight represents the humus.

The results for humus and humus ash are shown in the table along with the humus and ash by the official and original ammonium carbonate methods. All determinations here reported were made on the same solutions.

Method	No. 6185		No. 6187	
	Humus	Ash	Humus	Ash
Official.....	5.44	7.90	7.31	34.80
Ammonium carbonate.....	5.16	6.68	5.13	17.20
This modification.....	{ 3.80	0.18	2.70	0.10
	{ 3.68	0.40	2.75	0.18

The original ammonium carbonate method reduced the ash by about 15 per cent. in No. 6185 and by about 50 per cent. in No. 6187. This modification of the ammonium carbonate method reduced the ash in sample No. 6185 from 7.90 to 0.29 per cent., and in No. 6187 from 34.80 to 0.14 per cent.

The humus which was 5.44 per cent. in No. 6185 by the

official method was reduced to 3.74 per cent. by this modification of the ammonium carbonate method, and in No. 6187 was reduced from 7.31 to 2.73 per cent. The differences do not represent humus, but are probably entirely due to the loss of water on ignition of the hydrated clay and oxides of iron and aluminum.

The solutions obtained by this modification were free from all turbidity. It was found that with these soils the clay could not be filtered off and the aliquots were therefore removed with a pipette. The introduction of the ammonium carbonate increases the volume of the solution, and after standing over night, it is about 100.5 cc. This would make the results about 0.01 per cent. too low (in percentage of humus in soil). Since this is well within the limit of error with these soils, it is disregarded.

The Hawaiian soils studied are said to be of volcanic origin and are very rich in iron. Although the original ammonium carbonate method gives unsatisfactory results with these soils, we believe soils of this type will rarely be met with in the United States, since as stated before the method has given entire satisfaction on a number of the soil types of this country.

SUMMARY

The ammonium carbonate method for the removal of clay from humus solutions has given uniformly good results on a number of the soil types of the United States, but on exceptional soils, like some of those of Hawaii, a slight modification of the method is necessary to remove the clay. The modification consists essentially in increasing the amount of ammonium carbonate to 2 grams per hundred cubic centimeters, and heating for one hour.

TEXAS AGRICULTURAL EXPERIMENT STATION
COLLEGE STATION, TEXAS

LABORATORY AND PLANT

THE NEW HIGH FORM OF SULFURIC ACID CHAMBER

By F. J. FALDING AND W. R. CATHCART

Received January 20, 1913

Since the Sulfuric Acid Chamber-process has existed, the two important factors which have been uppermost in the minds of manufacturers, engineers, and chemists, are: *First*, economy of chamber space, which of course means economy of lead; and *Second*, economy of nitration. These economies have been accomplished in a very high degree and in a most satisfactory manner, by the use of a new form of lead chamber, which embodies a scientific principle heretofore ignored on account of a misconception of its importance.

HISTORICAL OUTLINE OF THE LEAD CHAMBER

The evolution of the Chamber-process is well known. At first intermittent—then continuous but without recovery of nitrogen oxides—next the addition of

Gay-Lussac towers, and finally the Glover tower.

The chambers, however, have been always simply a series of enlargements of the flue or gas conduit connecting, at first, the sulfur burners with the outer air or exit, and later the Glover and Gay-Lussac towers. These enlargements of the flue retarded the speed of the gases, permitting them to mingle and react.

As the chambers have been almost universally framed with timber construction, the height and width have varied principally in conformity with considerations of carpentry, a width of thirty feet and a height of twenty-four feet having been rarely exceeded; whereas a length of one hundred to two hundred feet or over, for each chamber, used to be quite common. Lead chambers have been constructed empirically, and of many shapes and sizes. Sometimes the gas would pass through from four to ten chambers in series having a total length of from four hundred to one thousand feet in all.

The principal dimension of the chamber space has been always the horizontal axis in the same direction as the travel of the gas.

¹ Covered by U. S. Patent No. 932,771 and Canadian Patent No. 124,132; owned by the Chemical Improvement Company, 220 Broadway, New York City. Also patented in England, Germany, France, Belgium and other countries.

It is an admitted observation that, irrespective of the length of the first chamber of a series, all the active work of such a chamber is performed within the first thirty or forty feet of its length. The remainder of the chamber is practically inactive, and reaction is not resumed until the gas has been again mixed by passing through a comparatively small flue or special apparatus in the nature of a surface condenser, when a new zone of activity is induced in a succeeding chamber. The condition existing in the first chamber is reproduced, but in a lesser degree of intensity, due to the diminished percentage of the sulfur dioxide content of the gas, as evidenced by a reduced temperature of the active zone. The same conditions with increasing reduction of activity apply to all subsequent chambers of the series, until the absence of sulfur dioxide in the final chambers sometimes actually permits

space. These attempts have been known as efforts "to reduce the chamber space." Among the schemes tried are the following:

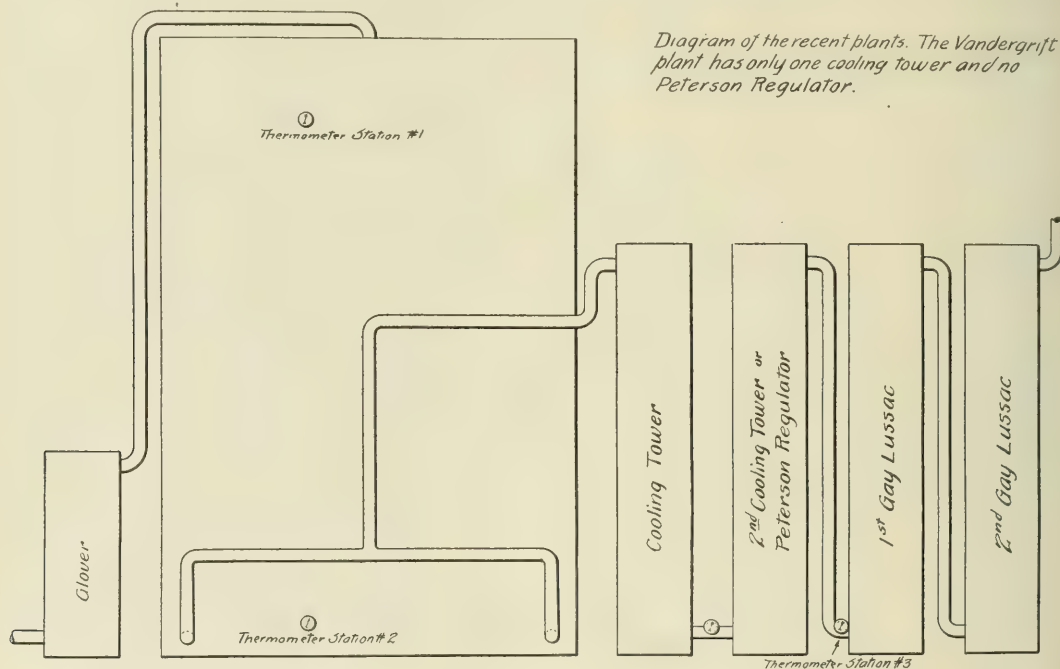
(1) The French "système intense," the principle of which is to increase the proportion of nitrous oxides to the sulfur dioxide in circulation—thereby increasing the speed of the initial reaction.

(2) Shortening the first chamber and passing the gas through surface or spray condensers before admission to succeeding chambers so as to increase the intensity of secondary reactions (Lunge plate columns, Gilchrist pipe columns, Hoffmann intensifiers, Pratt converters, etc.).

(3) Division of the initial volume of gas into two or more chambers in parallel instead of in series with a reduction of the secondary chamber space.

(4) The Meyer tangential admission of the gas into

Diagram of the recent plants. The Vandergrift plant has only one cooling tower and no Peterson Regulator.



the conversion of the nitrous gases into nitric acid and nitrogen peroxide, causing severe losses of niter and rapid destruction of the lead. It has even been the practice in some cases to admit a fresh supply of burner gas into the last chamber to counteract such conditions. (Benker.)

Mention should be made of the fact that, in earlier days, the chamber space consisted in some instances of a single, long, horizontal chamber, and, that the reaction was completed in this chamber, and to that extent was quantitative. This was accomplished, however, at so great an expense of chamber space relatively to the volume of gas reacting, that it was long since discontinued and a series of chambers adopted.

In recent years various attempts have been made to secure a quantitative reaction, or at least an intensive reaction in the first part of the chamber

cylindrical chambers working on the assumption that the spiral passage of the gas near to the cool chamber sides would accelerate the reaction.

Most of these propositions have produced considerable economies but none have been entirely successful. The first reaction has not been quantitative and the inert gas leaving the first zone of reaction has contained sufficient unoxidized sulfur dioxide to make succeeding chambers, with further zones of reaction of decreasing intensity necessary.

The first considerable alteration in the shape of the lead chamber was introduced by Dr. Theodor Meyer in January, 1900. To use his own words, quoting from a pamphlet issued by him at Halle in 1907: "A tangent chamber is a hollow cylinder of approximately the same diameter and height, whose feed pipe is attached near the top in the direction of a

tangent, and whose exhaust pipe is in the center of the floor of the chamber. An important factor in a large capacity is the height of the chambers (as I considered probably as early as 1900), for the highest capacity is shown by those two plants, whose chambers are highest: Griffith & Boyd, Baltimore, and Guilini Works, Ludwigshafen on Rh. (with 35 and 42 feet height). The height of the old oblong chambers has also been increased lately. Hartman & Benker built theirs up to 32.8 feet high. While this figure, however, is near the limit of profitable use of chamber-room (for oblong chambers), there is no such limit to the tangent chambers, for it is only necessary to keep width and height in proper proportion. If a chamber were to be changed into a tower the consequence would probably be a gradual retardation of

As regards the Benker chambers, Lunge¹ quotes from a personal communication from Benker, who states he "employs only narrow chambers, say 18 to 20 feet wide, and from 25 to 33 feet high. Such chambers are, in the first instance, better adapted for water spraying, but they also afford a better mixture of the gases, especially if the sides are cooled, by employing an open bratticing for the side passages (2½ in. laths with 1½ in. clear space) and a roof-rider. The cold gases descending along the sides must rise again in the center; but in the case of very wide chambers a dead space remains where the velocity is very slight, and where the mist of nitrous vitriol sinks down without acting on the gaseous constituents. Benker objects to Meyer's tangential chambers that there is no question of tangential action, that in the center of

ALGOMA STEEL CORPORATION, LIMITED—COKE PLANT DEPT., SAULT STE. MARIE, ONT.
Daily Report of Sulfuric Acid Plant, for 24 hours ending 7 A.M. Sunday, Dec. 29, 1912

Hour ending	Furnace Gas Per cent. SO ₂ Station 1	Niter (NaNO ₂) Pounds	Glover Bottom		Peterson regulator Percent. Na ₂ O ₂	Gay-Lussacs Percentage N ₂ O ₂		CHAMBER							Drips ° B.
			° F.	° B.		No. 1	No. 2	Temps. at stations, ° F.			Difference, ° F.				
								1	2	3	1-2	2-3	1-3		
8 A.M.	7.5	4	232	58	5.00	2.00	0.87	167	147	65	20	92	102	46½	
9 A.M.		4	232	58	5.00	2.00	0.87	165	147	67	18	80	98	46½	
10 A.M.	7.5	4	232	58	5.00	2.00	0.50	167	149	69	18	80	98	47	
11 A.M.		4	236	58	5.00	2.00	0.50	168	150	69	18	81	99	47½	
12 Noon.	7.5	4	237	58½	5.00	2.00	0.50	170	153	69	17	84	101	47½	
1 P.M.		4	237	58½	5.00	2.00	0.50	175	156	69	19	87	106	48	
2 P.M.	7.5	4	237	58½	5.00	1.86	0.50	176	158	69	18	89	107	48	
3 P.M.		4	237	58½	5.00	1.86	0.50	179	160	69	19	90	109	50	
4 P.M.	7.5	4	237	58½	5.00	1.86	0.50	180	160	70	19	90	109	50	
5 P.M.		4	236	58½	4.60	1.86	0.50	181	162	71	19	90	109	51	
6 P.M.	7.5	4	236	58½	4.60	2.00	0.45	183	162	72	21	90	111	49	
7 P.M.		4	236	58½	4.60	2.15	0.50	183	163	72	20	91	111	48	
8 P.M.	7.5	4	236	58½	4.60	2.15	0.50	183	163	72	20	91	111	48	
9 P.M.		4	236	58	4.60	2.15	0.50	183	163	72	20	91	111	48	
10 P.M.	7.5	4	237	58	4.60	2.15	0.50	184	164	73	20	91	111	48	
11 P.M.		4	237	58	4.60	2.15	0.50	185	166	73	19	93	112	48½	
12 Midnight.	7.5	4	237	58	4.60	2.15	0.50	186	167	74	19	93	112	48½	
1 A.M.		4	237	58	4.60	2.15	0.50	186	167	74	19	93	112	48½	
2 A.M.	7.5	4	237	58	5.00	2.00	0.50	186	166	74	20	92	112	48½	
3 A.M.		4	237	58	5.00	2.00	0.63	184	165	74	19	91	110	48½	
4 A.M.	7.5	4	236	58	5.00	2.00	0.63	182	163	73	19	90	109	49	
5 A.M.		4	235	58	5.00	2.00	0.63	175	159	72	16	87	103	48½	
6 A.M.	7.5	4	235	58	5.00	2.00	0.63	174	158	72	16	86	102	48	
7 A.M.		4	235	58	5.00	1.86	0.61	175	158	72	17	86	103	47	
Total.....		96													
Average, 24 hours.....	7.5		58		4.85	2.02	0.60	178	159	71	19	88	107	48+	

RAW MATERIAL USED
Name of ore—"Helen Mine."
Pounds charged in 24 hours—20,700
Per cent. NaNO₂ on S—burnt, 1.16
Per cent. S—40.34
Per cent. S available—40
Per cent. S in cinder—0.36 A.M., 0.4 P.M.

the spiral-movement toward the lower part. The best ratio is an approximate equality of diameter and height."
This proportion has been observed in all his installations. In the United States the Griffith & Boyd chambers are 33 feet diameter and 35 feet high and the chambers of the Mountain Copper Company in California are 39.4 feet wide by 42.6 feet high.
Again to quote from Dr. Meyer: "Aside from the small end chambers the most rational shape and size of a tangent chamber is a cylinder of 32 ft. to 48 ft. height and with a capacity of 28,000 to 72,000 cubic feet." This would give respectively a diameter of 33.5 feet and 44 feet.

these circular chambers gases of different concentrations get mixed up, and that they would be too expensive if the only proper way was followed, viz., building many small circular chambers in a set."
Neither in the case of Meyer or Benker does the question of the convection currents seem to have been seriously considered. Benker's chambers are of the long horizontal type 75 to 85 feet long and are arranged in a series of three chambers.
Meyer evidently considered that the question of height is merely a question of chamber space and says that "If a chamber were changed into a tower the consequence would probably be a gradual retardation"
¹ "Sulfuric Acid and Alkali," Vol. I, 3rd Ed., page 459.

tion of the spiral movement toward the lower part." He therefore increases the diameter in proportion with the height.

In this short history of the lead chamber, it has not, of course, been possible to mention all the forms of chambers which have been used at different times, but it is submitted that they all contain the same defect, in that they practically ignore the convection currents of the reacting gases, that they are all virtually enlargements of the horizontal axis of the flue and that they all involve a series of reaction zones of decreasing intensity.

The practical ignoring of the laws of convection is responsible for the comparative failure of the above described forms of chamber construction.

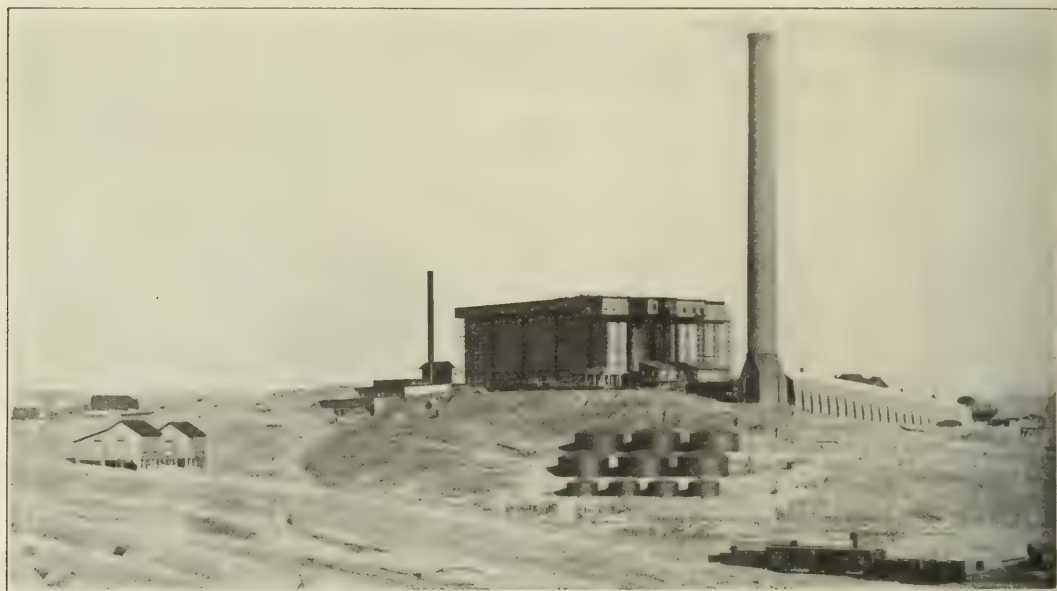
THE THEORY OF THE HIGH CHAMBER

The technical gas mixture admitted to a chamber

process. This 5 per cent. excess oxygen will be found in the exit gases.

During the passage of this gas mixture through the Glover tower the percentage of sulfur dioxide it contains is further reduced by partial oxidation to the trioxide (SO_3) and partly by the addition of nitrous oxides, and partly by water vapor derived from the evaporation taking place in the Glover.

The gas on leaving the Glover tower enters the lead chambers, and just at this point it is better fitted in every respect to react rapidly and quantitatively, than it will be at any subsequent stage of its passage toward the exit; and any means that can be devised for holding the active zone at this point, until the reaction is completed, and securing a rapid separation of the inactive from the active gas, permitting only the inactive gas to go forward to the Gay-Lussac



TENNESSEE COPPER CO. ACID CHAMBERS, SHOWING STORAGE TANKS (7000 TONS) AND GAS FLUE

sulfuric acid system is diluted with a large percentage of nitrogen. This nitrogen takes no active part in the chemical reactions, but absorbs and carries away a large amount of the heat of the exothermic reactions taking place in the chamber.

A good technical gas mixture, when produced from the oxidation of pyrite, will contain approximately, omitting minor impurities:

	Per cent. volume
Sulfur dioxide.....	7.5
Oxygen.....	9.0
Nitrogen.....	83.5
	100.0

Such a gas mixture will contain oxygen sufficient for the oxidation of the sulfur dioxide to the trioxide, and also provide the necessary excess of 5 per cent. of oxygen for the satisfactory operation of the chamber

towers and exit, will surely be advantageous.

Remembering that the gas mixture under consideration is dilute in active constituents and contains a large percentage of nitrogen which does not enter into the reaction at all, and that the reactions entered into by the active gases are strongly exothermic, it follows that if proper opportunity is given for the action of convection, there will result a rapid and complete separation of the heat-producing gases and the inactive and non-heat-producing gases.

To secure this separation by convection would clearly necessitate increasing the height of the chamber in relation to the horizontal sectional area so as to allow relative zones of reaction and inaction therein, the incoming gas being admitted to the zone of reaction, and the outgoing gas being drawn from the zone of inaction.

The horizontal sectional area of the chamber would have to be proportionate to the volume of gas admitted and the height proportionate to the time necessary for the quantitative reaction of such volume, and the gas travel would be vertically downward, subject to convection currents, instead of horizontally forward.

Bearing these considerations in mind, it becomes clear what may be the effect of increasing the length of the vertical axis of the chambers or, in other words, the height in relation to other dimensions.

The gas mixture, admitted to the chamber, immediately sets up a strong exothermic reaction. If the chamber is high, convection currents will be induced and the reacting gas will immediately tend to rise

THE RESULTS OF THE HIGH CHAMBER IN PRACTICE

The considerations which have been mentioned appeared to have such force, that in March, 1905, these views as to this high chamber construction were placed before the United States Steel Corporation, who were about to erect a sulfuric acid plant. They decided to adopt this construction and a plant was ultimately erected at Vandergrift, Pa., consisting of one chamber 50 feet square by 70 feet high, together with one Glover, two Gay-Lussacs and a small unpacked cooling tower 9.5 feet square by 50 feet high located between the chamber and the Gay-Lussac towers. This plant was put into operation on January 1, 1907, and the results amply justified expectations, and proved the following facts:

ALGOMA STEEL CORPORATION, LIMITED—COKE PLANT DEPT., SAULT STE. MARIE, ONT.

Daily Report of Sulfuric Acid Plant, for 24 hours ending 7 A.M., Jan. 19, 1913

Hour ending	Furnace gas Per cent. SO ₂ Station 1	Niter (NaNO ₃) Pounds	Glover Bottom		Teterson regulator Percent N ₂ O ₅	Gay-Lussacs Percentage N ₂ O ₅		CHAMBER							Drips. ° B.
			° F.	° B.		No. 1	No. 2	Temps. at stations, ° F.			Difference, ° F.				
								1	2	3	1-2	2-3	1-3		
8 A.M.	7.5	2	241	59	4.3	2.90	0.61	180	161	79	19	84	101	47	
9 A.M.		2		59				176	156	78	20	78	98	47	
10 A.M.	7.5	7	240	59	4.3	2.80	0.58	172	154	78	18	76	94	46½	
11 A.M.		5		59				174	154	77	20	77	97	46½	
12 Noon	7.5	4	240	59	4.3	2.33	0.57	174	154	77	20	77	97	46½	
1 P.M.		4		59				176	157	76	19	81	100	47	
2 P.M.	7.5	4	240	59	4.3	2.33	0.56	178	158	76	20	82	102	48	
3 P.M.		4		59				178	159	76	19	83	102	48	
4 P.M.	7.5	4	240	59	4.3	2.33	0.50	178	159	76	19	83	102	48	
5 P.M.		4		59				178	159	75	19	84	103	48	
6 P.M.	7.5	4	240	59	4.3	2.33	0.46	178	159	75	19	84	103	48	
7 P.M.		4		59				178	158	75	20	83	103	48	
8 P.M.	7.5	4	240	59	4.3	2.33	0.50	178	158	75	20	83	103	48	
9 P.M.		4		59				176	155	73	21	82	103	47	
10 P.M.	7.5	4	240	59	4.3	2.33	0.46	176	155	73	21	82	103	47	
11 P.M.		4		59				176	156	73	20	83	103	47	
12 Midnight	7.5	4	240	59	4.6	2.33	0.46	176	157	73	19	84	103	47½	
1 A.M.		4		59				176	157	73	19	84	103	47½	
2 A.M.	7.5	4	238	59	4.6	2.54	0.36	178	158	73	20	85	105	47½	
3 A.M.		4		59				178	159	73	19	86	105	47½	
4 A.M.	7.5	4	238	59	4.6	2.54	0.62	178	159	74	19	85	104	48	
5 A.M.		4		59				172	153	77	19	76	95	48	
6 A.M.	7.5	4	240	59	4.6	2.54	0.72	177	158	78	19	80	99	46	
7 A.M.		4		59				178	160	78	18	82	100	45½	
Total		108													
Average, 24 hours	7.5			59	4.4	2.47	0.55	177	157	76	20	81	101	47¼	

RAW MATERIAL USED

Name of ore—"Helen Mine."	Per cent. S—40.34
Pounds charged in 24 hours—21,000	Per cent. S available—40.00
Per cent. NaNO ₃ on S—burnt, 1.29	Per cent. S in cinder—0.32 A.M., 0.42 P.M.

DIARY

Chamber man increased soda from 4 to 6 lbs. during night. This was not necessary. Took it off first thing this morning.
The 172° top temperature at 5 A.M. was due to pump breakdown. Had no acid upstairs to run over Glover tower. W. E. T.

and to remain at the top so long as the reaction goes on, only the inert, non-reacting, non-heat-producing, and therefore cooler gases tending to return to the bottom of the chamber. If the relationship of the height to the area and the volume of gas admitted is correct, the reaction taking place in the chamber will be quantitative and the gas drawn from the chamber at the bottom will consist entirely of nitrous compounds and inert nitrogen with some oxygen. In other words, the process will be completed in one chamber and the necessity of further chambers (which cost just as much as the first active chamber) for more and more sluggish processes (or decreased efficiency in work done) will be obviated and a great economy in cost of chamber space will be secured.

(1) A large production of sulfuric acid with a minimum of chamber space.

(2) A quantitative reaction in the single chamber, the SO₂ being completely converted in the chamber itself as proved by tests at the chamber exit.

(3) An insufficiency of cooling capacity—the gases on leaving the cooling tower being too hot and too moist to permit the best work in the Gay-Lussac towers.

(4) That in spite of this insufficiency of cooling capacity a reasonable consumption of niter could be attained—i. e., an average between 2 and 3 per cent. of NaNO₃ based on the sulfur burned, while frequently for days together the consumption of NaNO₃ did not exceed 1.5 per cent. The insufficiency of

cooling capacity clearly interfered with a maximum output of product and a minimum consumption of NaNO_3 .

Before this plant had been completed, the Tennessee Copper Company, who were being pressed by the Government to abate the nuisance caused by the sulfur dioxide fumes produced in their copper smelting operations, decided to erect a plant at Copperhill, Tennessee, consisting of twelve chambers of the same dimensions as those at Vandergrift. This plant now consists of thirty-six of these chambers. The work, from a technical standpoint, is not perfect, as it entails a considerable consumption of NaNO_3 . However, the Company claims that their net profits from the production of sulfuric acid are equal to their profits from copper and other sources. This irregularity of working is due to the character of the smelter gases which contain from 4 to 6 per cent. of CO_2 , and in which the percentage of SO_2 fluctuates greatly.

a concentrating tower. No additional labor is involved in the concentration, and the fuel cost is represented by a consumption of 100 pounds per hour of a mixture of coke breeze and slack coal fed by means of a special smokeless stoker, or a consumption of less than 70 pounds of fuel per ton of 66°B. acid.

(2) For the Dominion Iron and Steel Company, Limited, at Sydney, Cape Breton, Nova Scotia, a chamber 50 feet square by 70 feet high; specified capacity in 24 hours, forty to forty-five tons of 60°B. sulfuric acid. This plant includes one Glover tower 10 feet in diameter by 26 feet high, two Gay-Lussacs 9.5 feet square by 50 feet high and two packed cooling towers of the same dimensions as the Gay-Lussacs, placed between the chamber and the Gay-Lussacs.

(3) For the Algoma Steel Corporation, Limited, at Sault Ste. Marie, Canada, a chamber 35 feet square by 70 feet high; specified capacity in 24 hours, twenty to twenty-five tons 60°B. sulfuric acid. This



TENNESSEE COPPER CO. SMELTER AND ACID PLANT

With the advantage of the data obtained at Vandergrift and Copperhill three plants have been subsequently erected as follows:

(1) For the Cleveland Cliffs Company, at its Pioneer Iron Works plant at Marquette, Michigan, one chamber 50 feet square by 70 feet high; specified capacity in 24 hours, thirty to thirty-five tons of concentrated 66°B. sulfuric acid. This plant includes one Glover tower 10 feet in diameter by 26 feet high, two Gay-Lussacs 10 feet in diameter by 50 feet high, and two packed cooling towers 10 feet in diameter by 50 feet high, placed between the chamber exit and the Gay-Lussacs. The pyrite used at this plant is a remarkably pure concentrate, practically free from dust and arsenic; and the arrangement of the towers is such that the hot Glover tower acid is run directly by gravity from the Glover tower at a temperature of 310° to 320°F. , by means of fused silica conduits into

plant is equipped with one Glover tower 8 feet in diameter by 25 feet high, two Gay-Lussacs 8 feet in diameter by 50 feet high, one packed cooling tower following the chamber exit and one Petersen regulator tower between the cooling tower and the Gay-Lussac, both these towers being of the same dimensions as the Gay-Lussacs.

Not one of the above installations has been made for a concern previously engaged in, or familiar with, the manufacture of sulfuric acid. In every instance the operatives are drawn from the ordinary labor available in the locality. In at least two cases the trained chemists in charge of the process had never previously seen a sulfuric acid plant. In view of these conditions, it is submitted, that the results of actual operation are entirely satisfactory. In each case (with the exception of the Tennessee Copper Company's plant, where for obvious reasons no regularity

could be assured) the consumption of niter of not over an average of three per cent. was stipulated, and also a minimum output as stated in the preceding paragraph. This output in terms of chamber space was as follows:

(1) One pound of sulfur to 7.8 cubic feet of chamber space;

(2) One pound of sulfur to 7.2 cubic feet of chamber space;

ANALYSIS OF RECENT TYPICAL DAILY REPORTS OF THE VANDERGRIFF AND ALGOMA STEEL CORPORATION SULFURIC ACID PLANTS

Averages—Daily reports, etc.	First Plant erected U. S. Steel Corporation Vandergrift (a) Plant brimstone	Last Plant erected Lake Superior Corporation Ltd. Algoma Steel (b) Corp'n Ltd. Plant pyrites—"fines" (Dec. 29, 1912)
Pyrites "fines" charged in 24 hours (pounds)...	20,700
Pyrites contain sulfur per cent.	40.34
Cinders contain sulfur per cent.	0.38
Sulfur charged (pounds)...	15,345	8,350
Sulfur available or burned (pounds).....	8,280
Per cent. of SO ₂ in gas...	10.4	7.5
Nitrate of soda—per cent. on sulfur charged....	1.56	1.15
Nitrate of soda—per cent. on sulfur burned....	1.16
Per cent. N ₂ O ₃ in Petersen regulator.	4.85
Per cent. N ₂ O ₃ in nitrous vitriol.....	2.60	2.02
Per cent. N ₂ O ₃ in final Gay-Lussac tower....	0.17	0.60
Temp. of gas—8 ft. from top of chamber(c)....	205° F.	179° F.
Temp. of gas—5 ft. from bottom of chamber....	190° F.	160° F.
Temperature of gas at entrance to Gay-Lussacs.	127° F.	72° F.
Difference of temperature between top and bottom of chamber.....	15° F.	19° F.
Difference of temperature between bottom of chamber and Gay-Lussacs.....	63° F.	88° F.
Drip—Degrees U. S. B....	46.5° B.	48° B.
Average strength of acid in chamber pan (U. S. B.).....	52 to 53° B.	53 to 54° B.
Average strength of finished acid.....	62° B.	58 to 59° B.
Dimensions of chamber (feet).....	50' × 50' × 70' high	35' × 35' × 70' high
Outside dimensions of towers—except Glover (feet).....	9'6" × 9'6" × 50' high	8' diam. × 50' high
Outside dimensions of Glover tower (feet)....	9'6" × 9'6" × 24' high	8' diam. × 24' high

(a) The Vandergrift Plant has been in operation some years and was the first of this character of plant built.

(b) The Algoma Plant has been operated less than three months.

(c) Temperatures taken on side of chamber with usual bent thermometer.

(3) One pound of sulfur to 6.4 cubic feet of chamber space, or a maximum output of one pound of sulfur to 6 cubic feet of chamber space, or a minimum output of one pound of sulfur to 8 cubic feet of chamber space, or an average output of one pound of sulfur to 7 cubic feet of chamber space. In all cases these specifications have been carried out and easily exceeded. The plants have been taken over and paid

for and are operating to the satisfaction of the owners.

TEMPERATURE OF REACTION IN THE HIGH CHAMBER

In the ordinary operation, readings are taken from the usual bent thermometers placed, the one about 12 feet from the top of the chamber in the side lead, and the other about 4 feet from the bottom of the pan, in the side lead. In practice the temperatures are read only on one side of the chamber. At first thermometers were placed on all four sides of the chambers, and not only near the middle of the sides, but also near the corners, until it was found that the variation in these thermometers at equal height in the chamber was practically nil.

When the chamber was first used, thermometers were placed also vertically 5 feet apart on all four sides of a chamber, and an extended series of readings taken, all of which showed a gradual diminution of temperature from the top to the bottom. This decrease in temperature, of course, was more rapid in the lower part of the chamber, but was distinctly marked after the first fifteen feet from the top, or the first two readings.

The difference between the upper thermometer (10 feet from the top) and the bottom thermometer will range from 22° F. to 7° F., according to the intensity with which the system is being driven, *i. e.*, the proportion of the amount of sulfur burned to the cubic feet of chamber space.

When the system is in normal operation, repeated tests show no more than the usual traces of SO₂ in the gases leaving the chamber. The packed cooling tower which follows the chamber serves to dry the gases leaving the chamber (by condensing the mist of sulfuric acid) before admission to the Gay-Lussac towers, and a further cooling of from 75° to 100° F. takes place in this apparatus, bringing the final temperature of the gases entering the Gay-Lussac towers to 60° to 80° F.

DRIPS

One drip reading has been found, by elimination, to be sufficient. This has been placed, by reason of convenience, near the lower thermometer about four feet from the bottom at the middle of the chamber side. If this drip is carried at 47°–48° B., the pan acid will be found invariably between 52° and 54° B. At one plant a table drip has been employed, and the readings respectively of the table drip, the side drip and the chamber acid as drawn to the storage tank, were 55° B., 47° B., and 53.6° B.

CONSUMPTION OF NITER

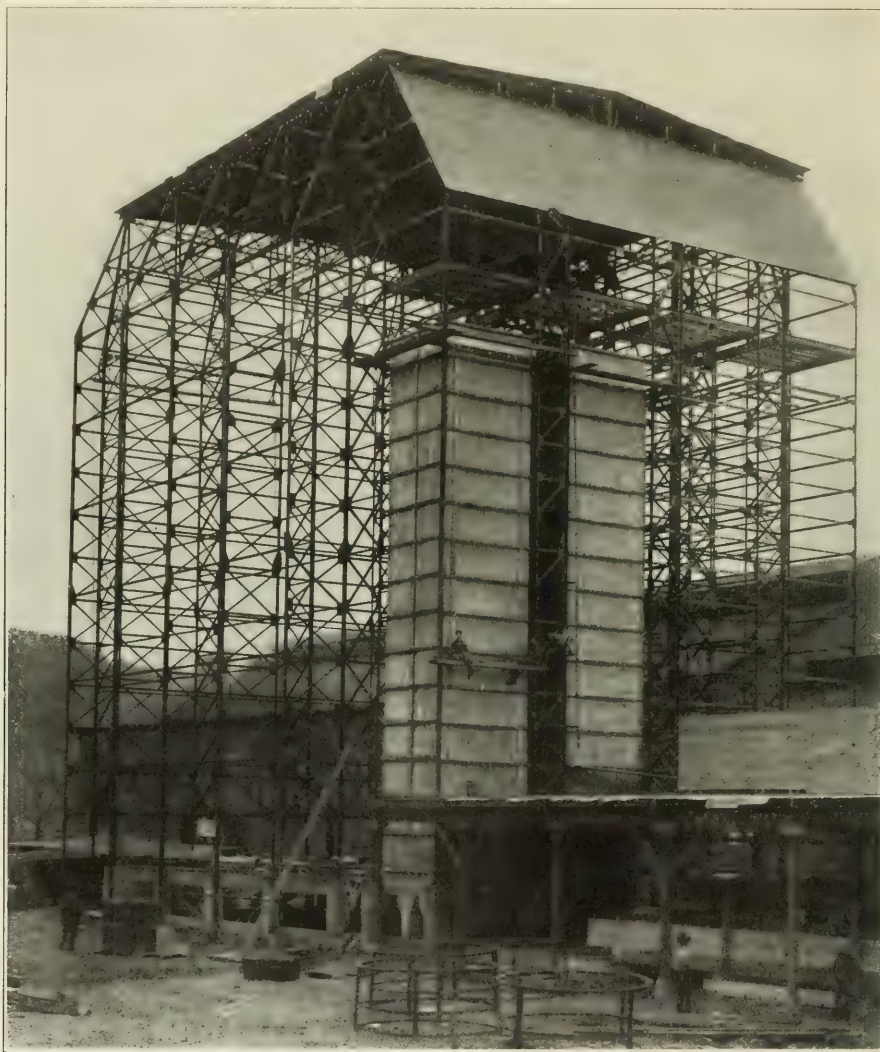
Some of these plants are of course not doing as regular work as they would do if operated by skilled labor. The consumption of nitrate of soda is frequently for considerable periods as low as 1 to 1½ per cent., a record which undoubtedly could be uniformly maintained by competent operatives (see tables).

THE ADVANTAGES OF THE HIGH CHAMBER

The advantages of this chamber are noteworthy: 1. *The Saving of Lead.*—For purposes of comparison,

take a chamber fifty feet square and seventy feet high, representing a capacity of 175,000 cubic feet (4952.5 cubic meters). This comparison has no reference whatsoever to the actual efficiency of such chamber space. The largest chambers which Meyer has built are probably those of the Mountain Copper Company, which he states are 12 meters in diameter and 13 meters high. These would therefore have a capacity of 1470 cubic meters

the top, and five feet at the bottom. The straps for the sides six-pound, and for the top seven-pound. (These straps consist of a five-inch strip of lead burned onto the chamber sides, and extending horizontally continuously around the chamber at vertical intervals of about 5 ft. The straps are then bolted by means of clamp bars to horizontal angles, in such a way that the side lead does not touch the support-



VANDERGRIFF PLANT IN COURSE OF ERECTION—TWO TOWERS NEARLY COMPLETED

each. Three chambers of this size would be required, together with a small chamber 9 meters diameter and 6.5 meters high to give the same capacity as one high chamber 50 feet square by 70 feet high. In actual construction the weights of lead used in this chamber are as follows:

The top and bottom, seven-pound lead; the sides, six-pound lead, rolled to eight-pound for two feet at

ing angles or posts at any place.) The total weight of lead, including everything in connection with the chamber, is 141,000 pounds. A corresponding plant, according to the Meyer system, would require at least 220,000 pounds of lead, while a plant of three chambers of equal cubic capacity, built according to the old rectangular, horizontal system, would require from 240,000 to 300,000 pounds of lead. The saving:

in lead, therefore, is from 35 per cent. to more than 50 per cent. for equal cubic capacity, even supposing that the high chamber space is not more efficient.

II. Greater Efficiency of the High Chamber Space.—An efficiency of chamber space representing from 6 to 7 cubic feet of chamber space to one pound of sulfur burned, without the assistance of any auxiliary apparatus such as surface condensers, needs no further comment.

III. Great Economy of Ground Area and Foundations.—The fifty-foot chamber, allowing seven feet to the outside of the building for the width of the trusses, occupies only 4,096 square feet, whereas in the case of the old horizontal chambers the same chamber space would occupy about three times this area, and the Meyer Tangential System would require from two to three times this amount, depending on the size of the chambers.

IV. Fire-proof and Storm-proof Construction.—The method of construction, being entirely of steel and reinforced concrete, is fire-proof and storm-proof. The cost of this construction is about the same or rather less for equal chamber capacity than what is considered a good type of construction of the old chamber plants, where wooden frames and buildings are used.

V. Economy of Labor.—The compact arrangement of this Plant reduces the amount of labor required to the minimum. For any Plant up to 100 tons of 66° B. sulfuric acid in 24 hours the labor is as follows (12-hour shift):

When using *brimstone*, one chamber man who is also day foreman, one chamber man who is also night foreman, one day burner man, one night burner man—four men in 24 hours.

When using "*finer*" *pyrite*, one or two laborers will be required to handle the ore and cinder, making a total of 5 to 6 men in 24 hours.

When using *lump pyrite*, additional men will be needed, depending on the construction of the lump burners.

The operation of the high chamber (towers, pumping, concentration, etc.) requires only one man per shift of 12 hours.

The scope of this article could scarcely be considered as including a detailed description of the methods of steel construction and lead work.¹ It is sufficient to say that the difficulties connected with the same have been solved in a most satisfactory manner, both with reference to protection against fire and storms, and the durability of the lead work. The plants which have been longest in operation have demonstrated that the item of repairs has been considerably reduced, being approximately only about 20 per cent. of the amount usually attending the horizontal chamber construction.

220 BROADWAY
NEW YORK CITY

TECHNICAL ACCOUNTING AND CHEMICAL CONTROL IN SUGAR MANUFACTURE¹

By DAVID L. JAVOLL, JR.

INTRODUCTION

For the technical supervision of the manufacture of sugar, whether from beet or cane or whether the purpose be to make raw sugar or refined granulated, the activities of the chemist may well be directed along three lines of endeavor.

First, The sampling and analysis of all raw material such as coal, coke and limestone or lime. Almost without exception in the beet industry and in exceptional cases with the cane, this includes the daily systematic valuation of beets and sugar-cane deliveries for purposes of purchase. Further, it will include the analysis of field samples to determine maturity of crop in general and the effect of certain influencing factors in particular districts.

Second, The frequent and rapid testing of initial material, intermediate products at the several "stations" of manufacture and the final products, together constituting what is known as "chemical control."

Third, The keeping of the sugar account and the daily calculation of the efficiency of the various pieces of machinery and of the several intermediate processes of manufacture.

Chemical control is essentially diagnostic in character and takes advantage of the knowledge we have of how the sugar-bearing material should behave at the "stations" as now interpreted through chemical tests and of what constitutes recognized, unavoidable losses, to put in the hands of the foremen in charge the proper data.

Successful sugar accounting calls for good organization first and conscientious, well-trained chemists to carry it out. Success or failure depends upon the presence or absence of suitable conveniences, accurate factory weights and measures, calibration of utensils and the exercise of great care in the sampling, sub-sampling, compositing and preserving.

In the beet industry the polarization is practically the true sucrose (with raffinose absent) while in the cane industry the polarization is never the true sucrose but is the algebraic sum of the several optical activities, of all the participating bodies, not removable by lead acetate. Therefore, in this article the term polarization or "sugar" signifies the polariscopic reading when reduced to terms of 26 grams of material in 100 metric cubic centimeters. Sucrose refers to the Clerget figure.

A few terms, peculiar to the cane industry, may well be defined here.

Normal Juice.—Strictly speaking this is the whole juice of the cane as it exists in the tissues, or the combined juice of all the mill units when milling without the application of water of Saturation. It still has considerable significance in cane work but none in the beet. It usually runs from 0.1 to 0.7 degree Brix lower than the so-called First Mill Juice; it is also lower in purity. Owing to its variability under changing conditions it should be determined by actual run, without water, at stated intervals.

¹ Paper presented at the Fifth Annual Meeting of the American Institute of Chemical Engineers, Detroit, December, 1912.

¹ Ingenieur Awe in an article on the construction of lead-chamber walls (*Z. angew. Chem.*, 25, 2523-2524 (1912)) describes a method of construction which was first used on the "Falding High Chamber" several years ago and has been continuously used since in all of the Falding installations.

It does not appear that a proper figure can be obtained in less than 1 hour's run. Its Brix, taken in conjunction with that of the mill raw juice, is used in calculating the extent of the dilution due to the water of saturation.

Mill Extraction.—The percentage of the sugar in the cane that has been removed by the milling process.

Retention. The amount of sugar in the form of commercial sugar, expressed in terms of percentage of the sugar obtained in the milling process.

Total Efficiency.—The total sugar in the form of commercial sugar expresses in terms of percentage of the sugar in the cane. It is the product obtained by multiplying the extraction by the retention.

Blanc. A product of vacuum-pan boiling upon very low products variously termed "filet" and "string-proof." It is not boiled to grain, but is made very concentrated and the density judged by pulling a small quantity out to form a "string" or rolling a small ball in cold water and noting the hardness.

It is the final boiling in all houses not provided with crystallizers, the product being set aside in storage for slow cooling and crystallization, for from two to three weeks or more.

A very brief account of the processes of sugar manufacture may assist in making clear the purpose of chemical control and scheme of sugar accounting. United States beet and Cuban raw sugars only are considered.

BEET SUGAR

The factories of the United States make standard white granulated sugar in one operation from the sugar beet, which has a sugar content of from 14 per cent. to 23 per cent. average for the entire crop or "campaign," according to territory, season and seed pedigree.

1. **DIFFUSION JUICE.**—The beets are washed and then sliced into strips $3\frac{1}{2}$ to 7 mm. wide and 2-4 mm. thick, with cross-section V-shaped and the sugar extracted by a highly developed process of diffusion, at definite temperatures, leaving behind the "pulp," of sugar content 0.25-0.30 per cent. There results a very clean, but dark colored liquor, warm to hot, of density 0.8-0.9 that of the original juice of the cosettes (sliced beets), which goes to duplicate tanks for measurement, after which it is forced by centrifugal pumps to tall, closed tanks.

2. **LIMING AND CARBONITATION.**—Lime to the extent of $2\frac{1}{2}$ per cent. to 3 per cent. of the beets or lime-saccharate as produced, both in the form of "milk" of 17° B., is added, while simultaneously the mass is brought to a definite, high temperature by injected steam and carbonic acid from the lime kilns is pumped in. At the precise moment of granulation of the precipitate of CaCO_3 , etc., judged wholly by the eye and corresponding to 0.1-0.14 per cent. CaO alkalinity, the mass is released to the pumps which serve the set No. 1 filter presses.

3. **THE FILTRATIONS.**—After issuing from the first set of presses under $2\frac{1}{2}$ atmospheres of pressure in form of a brilliant, pale straw-colored liquor, it goes to a second set of tanks for further liming and carbonitiation, where the alkalinity is brought to 0.015-0.025 per cent. CaO . It is then passed through a second set of filter presses and then "sulfured." The presses are clothed with duck or jute or both. The press cakes are washed with hot water (condensed) to a

definite sugar content, set No. 1 to 1 per cent., set No. 2 to 0.5 per cent., judged by applying a suitable hydrometer to the issuing "sweet waters."

4. **"SULFUR STATION" NO. 1.**—Bleaching by means of SO_2 gas takes place here, reducing the reaction to faint alkalinity, neutrality or faint acidity as occasion demands, but always to a definite figure. The process is perhaps invariably a continuous one.

5. **GRAVITY FILTERS NO. 1.**—Passing through these is preparation for evaporation under multiple-effect system.

6. **CONCENTRATION.**—By means of quadruple or quintuple effect the density is raised to 60° Brix, some ammonia is given off, lowering of alkalinity in the absolute but rising as result of concentration; some precipitate forms. "Thick juice" results.

The work is now in the "boiling" house.

7. **"SULFUR" STATION NO. 2, OR "BLOW-UPS."**—The reaction is here brought to the desired point, either faintly alkaline or acid and by careful test, in accordance with a figure that has been found to give the best results at that factory and particular district and often influenced by the season: 0.02 per cent. CaO (basis) is seldom exceeded either way. Acidity may be aided by phosphoric acid; alkalinity induced by lime or soda ash. The thick juice, like all products passing this station, is here "blown up" with injected steam and reduced to uniform Brix, quite generally 60° , to dissolve any grain, aid filtration and promote good boiling in the pan.

8. **GRAVITY FILTERS NO. 2.**—These serve all products in the intricate but systematic work of the "boiling" house such as thick juice, high and low wash and greens and melted sugar, removing all suspended matter in preparation for the pan-service tanks.

9. **THE MASSECUITE.**—This is formed in a vacuum pan working under 26-28 inches of vacuum and in masses of many tons.

The boiling to grain is carried out purely as an art by men who make it a profession. Of course, it is based entirely upon well-known scientific principles. It is essentially crystallization-in-motion, during which the product, constantly augmented in quantity by fresh injections of liquor, is resolved into grains of sugar and a more or less de-sugared mother liquor.

The final result of the process is judged upon the so-called purity test. The initial product from the beets generally carries a purity of 88; as the sugar crystallizes and is removed by the centrifugals the purity ratio necessarily lowers, thus becoming a measure of efficiency and of paramount importance.

The first boiling, followed by hot turbinating, gives, upon washing or "covering" with diluted liquors, white refined sugar, a "wash" of 90-92 purity and a mother liquor of 78-80 purity. A second boiling to grain, massecuite having 78-80 purity, discharging while hot to the crystallizers, cooling there with the aid of a helix and water jacket for about three days and then centrifugating, gives a yellow sugar and an exhausted molasses, purity 58-60. The yellow sugar is redissolved and boiled, variously combined, to white refined sugar.

If it is the intention to recover still more sugar from the molasses so reduced in purity that it will yield no more sugar by crystallization, the sugar may be precipitated by a large excess of one of the oxides of the alkaline earths.

In the United States lime oxid is used, in absolutely anhydrous and impalpable powder. Tricalcium saccharate results, later soluble in the saccharine juice to monocalcium saccharate.

10. THE COOLERS.—Under agitation the powdered lime is slowly sifted into the molasses previously reduced to 12–14° Brix, kept cool at a definite temperature meanwhile, until the density of a filtered sample indicates 6–7° Brix. It is then filter-pressed as quickly as possible.

11. SACCHARATE PRESSES.—The ordinary Kroog type of press produces 40 cakes of 1 inch thickness; the saccharate presses produce a much thicker cake, usually 2½ inches thick; they fill and wash readily. The product from the coolers is here separated into the saccharate of 86–98 purity and a mother liquor known as "press waste water" of 6–7° Brix and 10–20° purity, all from a 58–62° purity molasses. The washing with cold water alone or combined with its own higher "sweet waters" is continued until a liquor having a Brix of 2½ to 3° results and the purity of the last runnings mounts to 15–30. The total product of the washing is known as "wash water."

12. SACCHARATE AND SACCHARATE MILK.—The saccharate press cake is transported to the liming and carbonating station of the main factory process, in the form of milk, being discharged directly into tanks provided with stirrers, where it is incorporated with liquors brought thither from various parts of the factory and bearing from known small amounts of sugar to mere traces.

A separate sugar account is required for the saccharate process and the yield should be about 67 per cent. of the sugar charged to it, in the form of refined white.

CANE SUGAR

Raw sugar factories dealing with cane aim to produce a sugar that will keep during storage and transportation, of a sugar content that will bring the highest price for the total sugar output and to get as high a yield as can be proved to be economical in the final summing up of all the conditions.

It is generally conceded that an even 96° Ventzke polarization at the port of entry brings the highest profit. It is very probable that all other grades will soon be suppressed.

1. THE MILLING.—Heavy iron mills replace the diffusion battery of the beet-sugar process. The installation generally consists of three units (individual mills) placed in tandem and composed of three rolls each; there are intervening conveyors and the whole train is preceded by a crusher of two rolls.

The crusher serves to break the outer rind and the nodes, liberating at the same time considerable juice which flows to the bed plate of the first unit. The rolls are ponderous; 7 feet long by three feet in diameter may be taken as a type.

The cane gets two compressions in passing through each unit, being sustained by the "turn bar" as it issues from between the cane roll and the top roll and passed on to be caught by the bagasse roll and the top roll for the still closer compression.

The cane, not being laden with molasses-forming salts to the great extent that the beet is, the rupture of the cells is not attended with disastrous consequences. Naturally the ratio between the fiber of the cane entering any given unit of the tandem and that of the bagasse issuing therefrom, is a measure of the efficiency with respect to the amount of liquid expressed. Where water of saturation is applied, hot or cold, it is generally sprayed forcibly upon the bagasse as it issues from the unit next the last, at the point of immediate release from pressure; the imbibition of the thin juices is the further development of the water treatment and is simple and effective. As high as five units and a crusher or in all, seventeen rolls have been employed in one tandem.

The juices from the first and second units only enter the process of manufacture, *i. e.*, under a system of combined saturation and imbibition, and, united, constitute the mill raw juice.

2. MILL RAW JUICE.—Sometimes called diluted juice.

With respect to its purity it is considered to represent the original juice of the tissues of the cane.

It is either at factory temperature or a trifle above it, depending upon the saturation water temperature; it is charged with air, turbid from suspended albuminous matter, wax, insoluble salts, clay, and fiber—this even after being strained through copper or brass sieves of 15–19 perforations per linear inch.

It is pumped to tanks for measurements or weighing and is then limed. Where heavy liming with carbonation is not practiced (and I know of no factory in Cuba doing this) the juice is only neutralized.

3. LIMING OR "TEMPERING" THE JUICE.—This is generally accomplished in sets of three large tanks per tandem, one filling, one under treatment and one discharging. Repeated trials upon different sized tanks have shown a size corresponding to three hectoliters per ton of cane per hour to be advantageous.

Chemists carry the reaction of the juice generally about neutral to litmus paper. The subject can be said to have been scarcely attacked from the quantitative standpoint.

Continuous liming is practiced in some factories.

Lime and heat form clear juice and cachaza or "scum."

After liming, the juice is passed through heaters where the product may be even superheated if desired, depending upon whether it is desired to eliminate all the air by a "flashing" operation before complete settling. If the air is not eliminated a thick scum rises to the top at 95° C. called "blanket," a small portion sinks to the bottom, while the separation is being effected in so-called defecators varying in size from 35–100 hectoliters, net; the time for making one complete round of the defecators will be 60 minutes but capacity should be had for 90 minutes, to allow for

irregular liming; 15 per cent. of the time will be consumed in filling, emptying and cleaning.

Continuous settling is effected in the Deming process and in the Hatton defecators.

The slightly opalescent, straw-colored juice is generally run, without filtration, merely decantation continuous or interrupted, directly to the multiple effect.

It should be passed through fiber or gravity filters if for nothing more than to catch much cachaza that slips into the process intermittently. The decanted cachaza is washed by decantation in small tanks and then sent to frame presses for compression and sometimes washing. Evaporation is carried to 55° Brix in a cane house, to facilitate (1) settling and (2) avoidance of false grain.

The boiling of the meladura to grained massecuite is similar in principle to that carried out in a beet factory.

Cane products grain with great facility, while beet products sometimes present great difficulty, conditions brought about by the variance in the character of the non-sugars, purity remaining the same.

Generally three grades of grained massecuites are boiled where crystallizers have been installed, all upon a nucleus of original meladura which ranges in purity from 80-92, according to district and time of season. *First massecuite*, purity 80-84, yielding a sugar polarizing 97-98° Ventzke and a corresponding green syrup or molasses of purity 60-64. *Second massecuite*, purity 70-74; corresponding molasses, centrifugated hot, 48-54; centrifugated after limited cooling in motion, purity 40-46; resulting sugar, washed by water or liquors to 96° V. *Third massecuite*, purity 58-63; corresponding molasses (final product), purity 30-35; resulting sugar polarization depending upon treatment. This last massecuite, when at 35-40° C. and 4-5 days old in crystallizers, is generally centrifugated and the untreated sugar discharged into a mixer where high-grade molasses is incorporated with it and it is again centrifugated and washed to the degree desired, generally 96. This process is styled "mingling."

In factories not provided with crystallizers (which keep the grain in motion) the exhaustion of the product when it reaches the purity 48-54 must be accomplished "at rest," which is brought about by discharging the final boiling, boiled "blanc" to a Brix of from 88-91, according to conditions, into small iron wagons or into large tanks where it is allowed to cool quietly and crystallize spontaneously for from 12-21 days or longer.

(To be concluded in the April issue.)

A MODIFICATION OF THE PARR TOTAL CARBON APPARATUS

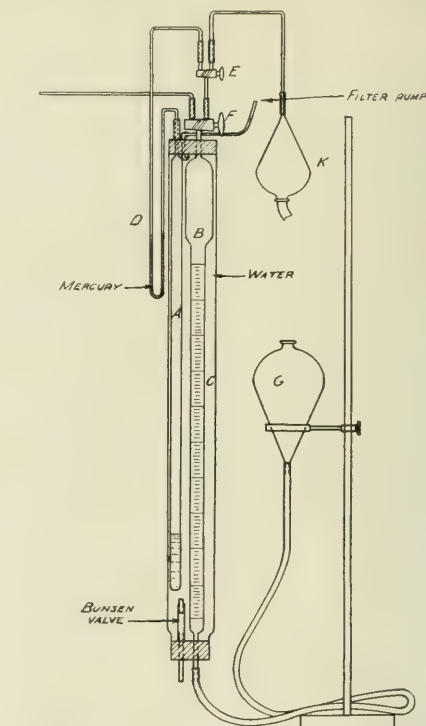
By C. E. MILLAR

Received December 13, 1912

The following modification, while used by the writer in connection with the Parr total carbon apparatus, is equally applicable to any gas burette. It has not only been found valuable as a time saver

but a great convenience since rapid changes of temperature and pressure are compensated for by the apparatus. When the amount of gas is sufficient to fill the pipette several times, as often happens in the determination of total carbon in soils, variation of temperature and pressure during the determination cause no trouble. In addition the long and tedious calculations necessary under former conditions in determining total carbon in soils and coals are reduced to multiplication of the pipette reading by a constant.

The diagram shows the modified portion of the Parr apparatus. When the sealed tube A is put in place and connected to B by means of D the heights of the



mercury columns in the arms of D are carefully marked. The barometric reading and the temperature of the bath C, which should be at room temperature, are also taken. It is obvious that B and G should be empty during the operation or else the core of one of the cocks E or F should be removed in order that the gas in A be under atmospheric pressure. The sealed tube A is filled to a depth of three or four inches with a portion of the same solution used in the pipette B. Since the two tubes are in the same bath the vapor pressure is the same when the height of mercury in the arms of D is the same.

When a volume of gas is collected in B it is allowed to stand until of the same temperature as C and hence of A. The stopcocks E and F are now opened so as to connect B and A. The leveling bulb G is adjusted until the level of the mercury in D is the same as when the apparatus was set up, in other words at the mark.

The volume of gas is now read and after absorption in the bulb K and drawing back into B, the process of leveling and reading is repeated in the same manner. These readings give the volume of the gas absorbed at the same molecular concentration as the gas in A when the apparatus was set up. The reading, therefore, need only be multiplied by the factor found to apply under those conditions.

In the bottom of the bath C there is a Bunsen valve which, by turning on the filter pump at the top, allows a current of air to pass through the bath C thus keeping the liquid well stirred. The tube D should be of small bore and of sufficient length to allow for the variations of temperature from season to season.

The above modification may be fitted to the ordinary Parr apparatus or gas pipette by inserting the stopcock E.

The writer wishes to thank Professor George H. Failyer for a suggestion that led to the above modification.

CHEMICAL LABORATORY KANSAS EXPERIMENT STATION
KANSAS STATE AGRICULTURAL COLLEGE
MANHATTAN

IMPROVED APPARATUS FOR TESTING THE JELLY-STRENGTH OF GLUES

By E. C. HULBERT

Received November 1, 1912

The apparatus consists of a thistle tube, the stem of which is twice bent and contains three bulbs. The two larger are about 2 cm. diameter and serve as safety traps; the smaller is accurately graduated to contain 1 cc.

Over the mouth of the thistle tube is stretched a

diaphragm of thin rubber. The far end of this tube connects through a 4-way stopcock with a gage consisting of a mercury filled U tube having its far arm extended upward and of smaller bore, this arm containing water or other liquid above the mercury. A rubber bulb is attached to one arm of the stopcock, the remaining arm being left open to the air.

The sample of glue-jelly is raised by means of the adjustable stand until the liquid in the bulb tube reaches the upper graduation *m*, and the

stand secured in this position, the stopcock meanwhile being set to connect arms A,B,C (see diagram). The cock is now turned to connect arms A,B,D and enough air forced into the system by means of the rubber

bulb, to force the liquid in the bulb-tube down to the lower graduation *n*, the cock turned to an intermediate position and the gage read.

The principal advantages of this apparatus over others are: The figure obtained is not influenced by the condition of the surface of the sample, such as formation of a tough "skin," rapid change of temperature during the test, etc. The error due to supporting a column of water resting directly upon the glue surface, as in another somewhat similar apparatus, is avoided; this is of especial importance in case of glues of low grade.

The reading is quickly made and may be repeated three or four times on the same sample, if desired.

No error is introduced either by the apparatus itself or its manipulation; duplicate samples, tested under like conditions of temperature, etc., give identical readings. The apparatus is simple and inexpensive and may be constructed by anyone having moderate skill in glass working.

Glues may be tested either under constant conditions of temperature and strength of solution, or compared with a standard glue.

The gage scale may be graduated in any convenient way, as by comparison with another type of glue testing apparatus, or with standard glues.

SULZBERGER & SONS CO.
KANSAS CITY, MO.

A USEFUL VALVE

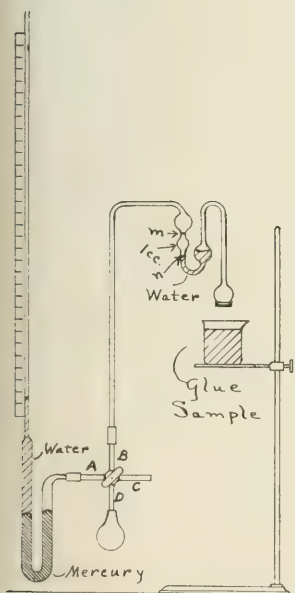
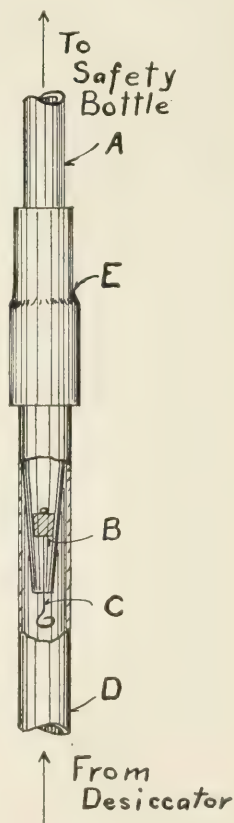
By NATHAN SMITH

Received November 15, 1912

This simple "home-made" valve has proved very efficient in preventing the "suckback" which usually results in vacuating desiccators by water suction, when the pressure is suddenly lowered. The valve may also be advantageously employed in the Kjeldahl nitrogen determination.

A small evenly drawn tube, A (the tip of an old pipette serves the purpose), is fitted with a piece of rubber, B, which acts as a valve. A piece of wire, C, is drawn through the center of the valve and bent as shown. Another piece of glass tubing, D, is fitted over the valve tube by means of rubber connection, E.

LABORATORY SCHIEFFELIN & Co.,
NEW YORK CITY



ADDRESSES

THE NEEDS OF THE MINING INDUSTRY

By J. E. CALLEBREATH¹

Received February 6, 1913

The two foundation industries of the United States are agriculture and mining. Agriculture is perhaps twice or three times as important as mining in the number of men engaged and in the value of its product.

Irrespective of their relative importance, one thing stands out preëminently and that is there can be no great agricultural prosperity without the prosperity of the mines. The population that depends upon the mines and the manufactured products of the mines supports agriculture.

Just the other day the Senate completed a piece of legislation which will give to the various State agricultural colleges the sum of three million dollars yearly for the extension of their work among the farmers. The bill was passed through both houses with comparative ease, as every one seems to have a thorough knowledge of the needs of agriculture. A report which accompanied this bill shows that the National Government has spent on the agricultural experiment colleges and experiment stations in round figures \$70,000,000; that it now spends \$3,940,000 in cash annually upon them; that Congress has appropriated each year \$15,000,000 for carrying on the exclusively agricultural work of the Department of Agriculture.

With the additional \$3,000,000 each year just granted, the total Federal aid given agriculture annually will be at least \$22,000,000. The result of this generous expenditure of money by the Federal Government for agriculture is seen in the phenomenal increase in production from year to year and the final bumper harvest of last fall.

These great appropriations for agriculture have been continued for years until to-day the officers of this department declare that a vast amount of valuable information is now in existence waiting some effective means of getting it into operation by the farming people of the United States. The plea for the additional \$3,000,000 was to take this information direct to the farmers.

What do we find the situation to be in regard to mining? The Bureau of Mines is getting one-half a million dollars a year, about as much money as is granted to the Department of Agriculture for the printing and binding of its publications. The Geological Survey, in existence many years, is now getting one million and a half dollars a year, a considerable part of which is used for the benefit of agriculture and other industries. This is a total of two million dollars of Federal aid for the great mining industry with its paramount unsolved problems—problems that are outside of solution by private parties.

In agriculture the men work in the open sunlight with a minimum of hazard to life. In mining nearly 700,000 men work in the dark caverns underground with a hazard that is not equaled in any other industry. The mines and quarries of the United States have an annual death roll of more than 4,000 men and 60,000 injured. This calamity of death leaves in its trail 2,500 or more widows and 15,000 fatherless children. It places upon the states the burden of caring for many of these widows and orphans, an amount that must be many hundreds of thousands of dollars a year.

We know from the experience of foreign countries that fully one-half of the number of deaths in the mines of the United States are unnecessary. We know that the work of the Bureau of Mines has reduced this terrible death-rate in the coal mines. The deaths in 1912 in the coal mines will be approximately 800 less than in the year 1907, when this work was first begun.

¹ Secretary of the American Mining Congress.

Practically nothing has been done by the Bureau in regard to the deaths in metal mines and the rate is heavier than in the coal mines. Neither has anything been accomplished in reducing the number of deaths in the quarries which have a still higher rate than the metal mines. This work can not be taken up until Congress and the people of the United States begin to have some adequate idea of the importance of the mining industry.

So difficult has it been in the past to obtain appropriations for this humane work, that those of us who are interested have learned to be extremely modest in the appropriations we have asked for. Only slight increases are asked for the coming fiscal year, when in fact the Bureau, on the basis of what it has already accomplished, can well spend two or three million dollars each year to the benefit of the entire country, rather than the one-half million which it now has.

Taking out of consideration the unusual hazard of mining and the fact that we are killing from three to five miners in this country each year where European countries are killing one and two, there is confronting Congress the question whether it will allow Western mining to languish and grow less with a diminishing number of men employed in each state, or give to the mining industry that aid which is similarly given to agriculture to rehabilitate this industry and increase the prosperity of the country. When I say that the Western mining industry is languishing, I have statistics to bear me out in the statement.

In 1906, in the states of Colorado, Montana and Idaho, the value of gold, silver, copper and lead produced reached a value of \$298,174,000. In 1910, the value of the production of the same metals in the same states was \$251,000,000, a loss of near \$50,000,000. In 1900 Colorado employed 40,000 miners; in 1910 that state employed 19,000 miners. In 1906 Montana employed 15,000; in 1910, 14,000 miners. In 1906, Idaho employed 7,000 miners; in 1910, 6,000 miners. In Colorado, in the year 1900 the precious metal production amounted to \$50,000,000; in 1910 the production was \$32,000,000. There is a definite reason for all this. The days of bonanza mining are gone and we are now down to the treatment of low-grade ores. This has led to a series of perplexing problems—the treatment of low-grade refractory ores as varying in character as the faces of the human family. In the Rocky Mountain States we have millions of tons of these low-grade ores containing practically billions of dollars in value.

The processes by which these ores may be reduced are more complex than any of the specialized problems you have on the farms. Their solution is beyond the reach of private capacity except in the rarest instances where large combinations of capital have succeeded in perfecting certain processes, which they keep to themselves.

These problems generally can be solved only through the aid of the Federal Government, and until they are solved the Western mining industry will continue to decrease in the value of production and the number of men employed.

The Bureau of Mines has asked for \$250,000 to begin work on such problems and to take care of the safety of the miners employed in these mines. If past experience is repeated, it will be with the greatest difficulty that the members of Congress can be shown the need for such an appropriation. In fact it will be more difficult to obtain the \$250,000 for this great industry than to obtain millions for agriculture.

I do not object to agriculture obtaining the increased yearly appropriation of \$3,000,000 for the extension of the work of the agricultural colleges in the states, but I am anxious to know why a bill introduced by Representative Foster, Chairman of the

House Committee of Mines and Mining, and which has the approval of the entire committee, calling for an expenditure of a maximum of \$1,200,000 yearly for mining schools in the various states, does not get an opportunity to come before the House for passage. I want to know why agriculture which has been so adequately cared for during many years can, with such ease, obtain \$3,000,000 additional funds for its work, while the bill for mining schools remains on the calendar, with the fear among its friends that it may not obtain sufficient support for its passage. I want to know how Congress is to look at the proposed appropriation for one-half million dollars for buildings for the Bureau of Mines at Pittsburgh, Pa. I may say that there is no department or bureau of the Federal Government so badly and so inadequately housed as the Bureau of Mines Experiment Station in Pittsburgh. The work is being conducted under the greatest difficulties in buildings belonging to the War Department, some of them nearly one hundred years old. Further, the War Department is anxious to regain possession of its property and has been continually notifying the Bureau of Mines that it must get out. Here is an emergency as far as the mining industry is concerned. What will Congress do?

I am heartily in favor of the increased appropriation for agriculture, but mining also has similar rights and greater needs.

There is no industry which adds so much per capita wealth to the country as the mining industry. There is no industry that, man for man, produces so much value to the country as the mining industry. It is an industry that must go hand in hand with agriculture. The prosperity of the country depends upon the success of both. Agriculture can not succeed without mining.

I am at a loss to understand why mining is so little appreciated in the United States when it attains such high commanding places in every other nation of the world.

THE CHEMICAL ENGINEER AND INDUSTRIAL EFFICIENCY¹

By W. M. BOOTH

The chemical engineer can take his legitimate place in industrial affairs only when he begins to concern himself with values and returns and can transmute the signs and symbols of the chemist to the dollars, cents and percentages of the business world. The profession must necessarily include men with diversified mental attributes, experiences and education. Natural inventors, builders, executives, analysts and economists are examples of the men who will choose this branch of engineering as a life work.

The first and highest type of endeavor concerns itself with the invention of new processes and the perfection of these, later establishing useful industries. Relatively few men have the ability, courage and means to embark in totally new enterprises, and the larger percentage of those who do so, fail, because these three important elements are not properly balanced.

Not less important, but demanding a different type of mind, perhaps more strongly analytical in its nature, is the large and ever-increasing field open to those who are able to improve or effect economies in the processes of firms already established. Closely related to this is the examination of new enterprises that seem to have merit and which need scientific assistance and capital for development. No greater damage has ever been wrought on American investors by any class of men than by the "new chemical," "private," or "Secret process" promoters who have used the subtleties of the science as a basis for fraud.

Irrespective of the particular division of endeavor undertaken, the chemical engineer must fortify himself against all classes of misrepresentation, and must concern himself with questions of process, cost, market, location and actual capital needed in any new industrial enterprise. No considerable investment should

¹ Paper presented at the Fifth Annual Meeting of the American Institute of Chemical Engineers, Detroit, December, 1912.

ever be made without a complete report from conservative men, who are familiar with the industry involved.

While the basic operations of activity include agriculture, mining, transportation and manufacturing, the latter is chosen as best exhibiting the use of the chemical engineer along the lines previously pointed out.

Those who have made a careful study of the splendid papers of Dr. Munroe¹ and Dr. McKenna² to be found in the proceedings of this Institute have been impressed with the fact that nearly all of the manufacturing of the United States is carried on east of the Mississippi River, and that more than one-third of this is confined to New York, New Jersey and Pennsylvania. The following census report shows the increase in capital and people employed from 1850 to, and including, 1909:

	CAPITAL INVESTED IN MANUFACTURING	EMPLOYEES
1850.....	\$ 533,245,000	957,059
1860.....	1,009,856,000	1,311,246
1870.....	1,694,567,000	2,053,996
1880.....	2,790,273,000	2,732,595
1890.....	6,525,051,000	4,251,535
1900.....	9,813,834,000	5,306,143
1910.....	18,428,270,000	6,615,046

It will be seen that the investment at the latter date amounts to eighteen billion dollars and the number of employees to over six millions. To maintain the almost perpendicular increase in our manufacturing activities is the duty of the commonwealth, for no more useful type of industrial activity can be found, especially when our products can be placed in foreign markets at a profit.

The observations covered by this paper are necessarily personal and have accumulated during twenty years, ten of which have been devoted mainly to the questions now to be discussed. The observations cover fifty-three "going" plants, representing thirty-seven industries, and some others that have never gone further than a prospectus distributed by an ignorant or a dishonest promoter. Obviously, in a paper of this kind, a general outline only can be given.

In looking back over the years covered, it would seem as though the period has been one of unexpected crises—rising wages, unsettled market conditions, and acute competition. Among the fifty-three concerns above mentioned, there have been eight failures, two have withdrawn from business and one, only, has burned. The remaining industries are owned as follows:

Private	11
Corporations	19
Trusts	12

The failures were attributed to the following causes:

- Two to incorrect conceptions of the costs and profits of a business.
- Two to dishonest employees.
- Two to incompetent supervision.
- One to insufficient working capital.
- One to manipulation of the stock in New York City in 1907.

The superintendents of twenty plants have been forced out or discharged for reasons such as inattention to duty, incompetency, lack of knowledge of the business, trust management, the introduction of new methods, inability to pay dividends on inflated stock issue, dissention among officers of the company or inability to handle help.

As I understand the matter, a general efficiency survey of any business must recognize the following conditions:

EXTERNAL.

Policy of the government toward an industry: Capital upon which dividends must be earned.

Location.

Cost of plant and equipment.

¹ "The Chemical Industries of America," Chas. E. Munroe, *Trans. Am. Inst. Chem. Eng.*, **2**, 84.

² "The Centering of Great Industries in the New York Metropolitan District," Chas. F. McKenna, *Trans. Am. Inst. Chem. Eng.*, **2**, 65.

INTERNAL

Unit cost of finished product, subdivided as follows:		
Raw materials	Supplies	Fixed charges
Labor	Office expenses	Interest
Power	Repairs	Depreciation
Lighting	Sales	Insurance
Heating	Advertising	Taxes
Cartage, freight and express	Charity	

Considering the capital invested, and the importance of the manufacturing business to all the people, laborers, tradesmen and stockholders, the Government is bound to respect, foster and protect these interests at all times. It would manifestly be suicidal to introduce any highly protected industry into the United States pending our tariff changes.

The passing of the pioneers who built and operated our first mills has thrown the responsibility of ownership upon the shoulders of many men totally unfitted by experience or temperament to carry on the business. To add to this misfortune of inheritance, all basic industries have expanded enormously, requiring more capital than one family or group of men could furnish. This led to the general adoption, between 1880 and 1900 of the corporate idea. While of the greatest value as an industry builder, no more pernicious influence has entered the manufacturing business than this conception and use of an artificial individual without responsibility.

Abundance of money in the banks, the abuse of personal credit, and easy bankruptcy laws have made it possible to squander the public's money without scruple. In several instances in my experience, good operating managers have attempted to maintain their profits on an inflated and unwarranted stock issue, and have failed. Good men, improved machinery and low operating costs cannot offset unnatural

	Per cent.
Printing and publishing.....	20.33
Agricultural implements.....	11.09
Automobiles, including bodies, etc.....	22.03
Boots and shoes.....	15.47
Brass and bronze products.....	12.25
Bread and other bakery products.....	25.86
Butter, cheese and condensed milk.....	23.23
Canning and preserving.....	13.09
Carriages and wagon and material.....	12.14
Chemicals.....	15.45
Clothing, men's, including shirts.....	20.29
Clothing, women's.....	33.03
Confectionery.....	23.12
Copper, tin and sheet iron.....	10.72
Cotton goods, etc.....	8.66
Flour mill and grist mill products.....	16.32
Foundry and machine shop products.....	10.23
Furniture and refrigerators.....	11.66
Hosiery and knit goods.....	15.42
Iron and steel, blast furnaces.....	5.90
Iron, steel, steelworks, etc.....	9.38
Leather goods.....	16.73
Leather, tanned, curried and finished.....	6.75
Liquors, distilled.....	12.83
Liquors, malt.....	10.68
Lumber, and timber products.....	13.82
Marble and stone works.....	15.87
Oil, cotton seed and cake.....	12.04
Paint and varnish.....	13.40
Patent medicines, etc.....	28.28
Petroleum, refining.....	8.24
Silk, etc.....	13.18
Slaughtering and meat packing.....	15.02
Smelting and refining copper.....	21.25
Smelting and refining lead.....	5.29
Sugar and molasses (not beet sugar).....	7.15
Tobacco manufactures.....	20.71
Woolen, worsted and felt goods, etc.....	10.98

net from 20 to 60% annually, and two good years have often paid for plant and equipment complete. Government statistics of manufactures included in the Thirtieth Census reports show the average net returns, for the year 1909, on thirty-nine of the principal manufactures in this country (see preceding table).

Considering now the matter of location, the manufacturer generally follows his market. As the growth of the population of the United States is westward, it has been found expedient to move whole industries from Massachusetts and New York to Michigan, Illinois and Missouri. Relocation of furniture and wagon plants has been quite general, because it has been found cheaper to ship the finished product to the markets than to bring the raw material east. Changes in market conditions have compelled the agricultural implement manufacturers to locate in the middle west. Formerly the manufacture of shoes was a Massachusetts industry; now, whole towns in New York and Missouri are devoted to this business.

No better illustration of economic change can be cited than the conditions at my own birthplace, a valley south of Utica, New York. On a stream furnishing from 60 to 120 H. P. at each plant, sixteen mills were in operation from 1873 to 1885. These employed about 2000 people. Forks and hoes were made in two plants, wagons in one, woolen cloth in two, cotton cloth in five, knit goods in one, silk in one, paper in two, and sewing machines and mowing machines in one. The movement of freight and finished products kept the railroad and scores of teams busy. Furnishing provisions for the employees in the mills afforded a living for many tradesmen.

One agricultural implement plant was burned; one was bought by a trust and closed; the paper mills have been idle for years; three cotton mills have gone out of business; one woolen mill was burned and the other was closed; the knit goods plant and the machinery plant burned; and the silk industry was moved to Philadelphia. To-day, there are only three really good companies operating in the valley. Originally humming with the whirr of spindles and clicking with the throw of the shuttles in the looms, the valley is now quiet, and agriculture is the main business. Those of us who lived there did not know why so many fires took our industries away. It was observed that no factories were rebuilt. I now know that it no longer paid to make woolen and cotton cloth, to spin silk, and manufacture paper in that locality. The peculiar elements which we term economic conditions took our prosperity away, with incalculable loss to all concerned, stockholders, employees and tradesmen alike. The moss-grown walls to be seen on many swiftly moving streams are monuments that mark industrial change.

Capital is sometimes invested in new projects, the aim of which is the use of raw materials that are supposed to be abundant, but that are later found to be insufficient in quality or quantity. Cement plants along the Erie Canal in New York State represent this class and also illustrate the rapid changes that may enter the elaboration of a product. In this instance the use of shale rock has taken the place of marl and clay in the manufacture of cement.

Beet sugar factories were started at Lyons, Binghamton, and at Rome, N. Y. The cost of the plant in each instance was very large, people cheerfully investing their money and expecting unusual returns. After several years of failure and loss the entire project has been given up; the empty buildings now remain after an expenditure of not less than \$2,000,000. Colorado and California produce beet sugar at a profit. The location of the industry in New York state was a mistake, but the stockholders had to learn this. In the meantime, canning factories have sprung up throughout central and western New York and the well managed ones are in a flourishing condition. Cheap raw materials, plenty of help, excellent transportation facilities and a ready market are contributory causes to its success.

No science or art can determine with accuracy whether

overhead expense. "Good will" has no place on the balance sheet of a well regulated and solvent business. Any venture in the elaboration of raw materials ought, when brought to a paying basis, to be able to return to the stockholders a net profit of at least 10%. Some old established lines of business

economic conditions are correct for the location of an industry. Accident or good business judgment may accomplish what statisticians and scientists cannot.

COST OF PLANT AND EQUIPMENT

With plenty of money at his disposal, the optimistic manufacturer is apt to spend too great a portion on buildings and equipment. Ample working capital should always be held in reserve. The amount thus employed will necessarily vary with the business, but from 25 to 50% is commonly set aside for this purpose in smaller industries, the capitalization of which is from \$50,000 to \$200,000.

It is much better to build a plant in a modest way, anticipating growth, than it is to find capital for running a concern in the midst of business expansion; especially so, if stockholders have had to wait from three to five years without dividends.

Again, a very expensive plant may be erected with consequent large overhead expense, where the income does not warrant the outlay. I found it impossible to recommend the erection of a water-gas plant in a town of 3500 people. A canvass of all prospective users showed that not more than two or three per cent. income could be expected. A similar plant in a town of about this number of people can positively pay no more than two per cent. on the investment after all avenues for gas consumption have been thoroughly exploited.

LOCATION

To aid those who wish to study the problems concerning location, I have made a list of the elements that seem important. These are as follows:

Accessibility of raw materials	Climate
Market	Hygienic conditions
Transportation	Taxes
Labor	Insurance
Power	Banking facilities
Water	Heating
Supplies	Lighting

Obviously, all of these details cannot be discussed in a general paper. The importance of one item, water, is taken up in another paper to show how carefully capital should investigate a new location, when the growth of a business warrants a change or when misfortune requires it.

With a favorable location, a demand for the product, an honest stock or bond issue, a modest initial outlay for buildings and equipment, and sufficient capital for doing business, an executive should earn a fair dividend on the investment.

INTERNAL UNIT COST

The ideal is the basis of our best effort everywhere. In manufacturing, this deal is approached when the largest quantity of good goods is turned out at the lowest possible cost. To determine how to attain the above conditions is the duty of every executive. But the task is not a simple one, for book-keepers are not statisticians and although all of the data necessary in connection with the proportioning of expense in the manufacture of an article may be derived, it takes a large amount of study to draw correct conclusions. No simpler expedient in my estimation has been devised in this connection than unit cost. What does it cost to produce a pound, a horse power, a barrel, a yard, or a machine, any single article, many of which are made each month or year? These items may be apportioned as percentages. The separate items under fixed and operating expense become factors of the total. As an example, we will say that the production of a machine has entailed an outlay of \$25.00 and that this is divided as follows:

	Per cent.		Per cent.
Raw materials.....	20	Repairs	1.3
Labor.....	40	Sales.....	10
Power.....	7	Advertising.....	5
Lighting and heating.....	1	Charity	0.2
Transportation.....	3	Interest, depreciation,	
Office expenses.....	2.5	taxes and insurance....	10

This outline shows at a glance that labor is a large item in the cost of this article and that any economy that can be effected in this department will make an appreciable saving in the total outlay.

Through the kindness of Mr. E. Durand, of the Bureau of Census, I am able to present a comprehensive table illustrating the method above outlined:

STATISTICS OF MANUFACTURE THIRTEENTH CENSUS, 1910, PAGE 30
PER CENT. OF TOTAL EXPENSES REPORTED

INDUSTRY	Salaries	Wages	Materials	Miscellaneous expenses
All industries.....	8.1	18.6	65.8	10.5
Agricultural implements.....	8.6	24.3	51.1	16.0
Automobiles, including bodies and parts.....	4.5	23.1	62.5	9.9
Boots and shoes, including cut stock and findings.....	3.9	20.6	69.6	5.9
Brass and bronze products.....	4.1	17.3	72.6	6.0
Bread and other bakery products.....	4.0	17.4	69.9	8.6
Butter, cheese and condensed milk.....	1.4	4.3	91.0	3.3
Canning and preserving.....	5.6	13.5	72.0	9.0
Carriages, wagons and materials.....	5.7	27.0	58.9	8.4
Cars, general shop construction and repairs by steam R. R. companies.....	4.3	44.7	49.2	1.8
Cars, steam railroad, not including operations of R. R. companies.....	4.3	23.0	66.7	6.0
Chemicals.....	6.5	15.0	68.2	10.3
Clothing, men's, including shirts.....	5.2	20.7	57.9	16.2
Clothing, women's.....	6.0	23.0	61.1	9.9
Confectionery.....	7.6	13.1	67.9	11.4
Copper, tin and sheet iron production.....	5.8	22.4	63.7	8.1
Cotton goods, including cotton small wares.....	2.6	24.0	66.9	6.5
Elect. mach., apparatus and supplies.....	10.0	24.5	53.8	11.7
Flour mill and grist mill products.....	1.5	2.6	92.8	3.1
Foundry and machine shop production.....	8.7	29.8	50.1	11.4
Furniture and refrigerators.....	7.3	30.8	51.0	10.9
Gas, illuminating and heating.....	10.9	18.4	46.2	24.5
Hosiery and knit goods.....	4.4	25.5	62.7	7.4
Iron and steel, blast furnaces.....	1.8	6.8	88.4	3.0
Iron and steel, steel works and rolling mills.....	2.9	18.3	73.9	4.8
Leather goods.....	7.2	19.3	64.6	8.9
Leather, tanned, curried and finished.....	2.2	10.5	81.2	6.1
Liquors, distilled.....	1.0	1.6	18.4	79.0
Liquors, malt.....	7.6	13.7	32.2	46.5
Lumber and timber products.....	4.8	32.0	51.0	12.2
Marble and stone work.....	6.7	44.8	39.4	9.1
Oil, cottonseed and cake.....	3.1	4.3	87.7	4.9
Paint and varnish.....	9.3	7.4	71.1	12.2
Paper and wood pulp.....	4.0	17.2	69.7	9.1
Patent medicines, compounds and druggists' preparations.....	14.9	8.7	44.1	32.4
Petroleum, refining.....	1.8	4.4	89.6	4.2
Printing and publishing.....	16.7	26.6	32.6	24.1
Silk and silk goods.....	4.2	21.8	60.8	13.2
Slaughtering and packing.....	1.5*	3.9	91.3	3.3
Smelting and refining, copper.....	0.7	3.8	94.4	1.1
Smelting and refining, lead.....	0.9	3.4	94.8	0.9
Sugar and molasses, not including beet sugar.....	0.9	2.8	92.6	3.7
Tobacco manufactures.....	4.6	19.0	48.4	28.0
Woolen, worsted and felt goods and wool hats.....	2.6	18.7	72.9	5.8
All other industries.....	6.4	21.1	62.1	10.5

This is a valuable guide in any efficiency study of production costs, although too many items are grouped under expense, which may be used by any executive to conceal exorbitant bills of any nature.

The actual cost of a case of tinned goods of the season of 1912 is divided as follows:

	Per cent.		Per cent.
Raw materials ..	30.40	Interest.....	1.90
Labor.....	14.40	Depreciation.....	1.80
Fuel.....	0.17	Taxes and insurance.....	1.60
Freight and express.....	0.04	Boxes and labels.....	7.30
Maintenance.....	4.80	Loss on seed.....	5.80
Sales.....	3.90	Discount and brokerage.....	3.10
Advertising.....	0.90	Expense.....	8.70

The remaining items are not considered useful in this paper. The tin container itself includes a cost of 85% for materials and 15% for labor.

A woolen mill owner and operator furnishes the following table:

MATERIALS	LABOR	EXPENSE
Raw stock	Office	Insurance
Soap	Factory	Taxes
Dyes	Overseers	Charity
Wool		Executive salaries
Coal		Depreciation
Wool oil		Repairs
Cotton and shoddy		

Percentages were not given but the total annual expense, including the three subdivisions above shown, is divided by the number of yards of cloth turned out to determine the cost price per yard.

I am familiar with the actual cost of reducing a ton of garbage by the naphtha process. This, on a percentage basis, is as follows:

	Per cent.		Per cent.
Labor	47.43	Superintendent	3.97
Coal	20.81	Taxes	0.45
Pressing	12.37	Interest	0.28
Filter cloth	2.89	Office	0.24
Gasoline, oil and light	8.00	Commission and anal-	
Freight	1.77	yses	0.74
			99.94

Labor is shown to cost an excessive amount. The gasoline item needs investigation.

The following elements compose the cost of a small copper instrument:

	Per cent.		Per cent.
Labor	61.62	Paint	0.22
Raw materials	27.41	Screws	0.22
Burner	6.03	Lacquer	0.55
Hanger	1.31	Bolts	0.33
Polishing	1.64	Solder	0.11
Support	0.54		

Obviously the labor cost of the instrument is excessive.

The official having charge of the cost department should ascertain at fixed intervals, by inventory and from records, the exact unit cost of any or all articles produced. This information should be made a part of a blue-print chart, carrying at the left a list of the items composing the record and a continuous line, showing the fluctuations in the cost of each, from month to month. If any one of these lines arise from causes beyond the control of the management, others must fall if the price of the finished article is to be maintained. Heating and lighting will fluctuate with seasonal changes; interest and depreciation, charity and office will remain practically horizontal. Unless the industry controls its own raw materials these usually increase in price; labor of all kinds increases; power is more expensive because coal is higher in price and water power has, in many plants, been replaced by steam. There is a very gradual rise in transportation costs and in supplies; taxes and insurance are constantly increasing everywhere.

With such records available, the operating manager is able to determine where efficiency methods could be applied to advantage.

In a former paper before the Institute, I have discussed "Power" from a percentage basis. Since that time, the use of electricity has become quite general and the H. P. year cost has been considerably lowered in a large number of plants.

STOCK AND SUPPLIES

The raw materials needed in operations of the manufacturer are usually closely bought and economically handled. I have

found this particularly true in woolen, cotton and paper mills.

Every successful enterprise requiring raw stock must include an expert buyer of large experience, whose business it is to make a study of market conditions and fluctuations. Ten years ago, much more practical experience was required to fill such a position than at present. This has been brought about by the general introduction and use of specifications. One by one, natural products have been standardized; coal, wool, cotton, ores, oils, paper stock, iron and steel and natural earths; these are a few of the hundreds of raw materials used by manufacturers. Physical and chemical standards have been set to replace the guess and estimation methods that came from experience and that are often wide of the truth. A relatively inexpensive man who has a testing laboratory at his disposal can determine the actual value of raw stock much more accurately than some high-priced man can guess at it. Two items on our cost sheet can be turned downward and kept there at relatively small expense.

Unless the specification idea is carried throughout the mill to include the finished product, the work is incomplete, for the adoption of such a system invariably improves the quality of the goods turned out. For example, every piece of wood, of composition and metal that goes into an automobile or locomotive should be of the best quality, proved to be so by actual experiment. This rule holds for manufactured products generally.

One of the weakest points in the personnel of the mill organization to-day is the purchasing department. I refer more particularly to those in charge of the purchase of the supplies. This important branch of the business is often left to incompetent clerks, who antagonize salesmen generally and who buy from men from whom they get the greatest possible return—gifts, dinners, an occasional trip, or even money. Honest traveling men avoid such purchasing agents, to the permanent loss of the business.

A shrewd salesman may spend from six weeks to six months in placing an order for expensive equipment that a concern never needed and should not buy. In my experience, men totally remote from the ordinary purchase of supplies should be employed in connection with new and valuable equipment. Consulting engineers can act to good advantage, turning in reports that show the general market conditions, kinds of apparatus or material available, with the experience obtained from the use of these in other plants.

SUPPLIES

Every manufacturer uses mixtures and compounds, the exact nature of which he has no knowledge: oils, dyes, fillers, adhesives, cleaning agents, waxes and polishes, powders and salts. In some instances, such materials have a total cost of \$2000 per month. Many simple substances are sold in large quantities, at inflated prices. For one concern, I was able to lower the cost of a special substance bought for \$50 a ton by substituting the same material from another source at \$15 per ton. Good business requires a knowledge of supplies and their component parts, for the purpose of keeping the cost down, for the protection of workmen, and to guard against fire.

No feature of factory economy should be as closely watched as the storeroom. A storekeeper should be in charge every moment of the working day, and should be held responsible for all stock handled, distributing this over a counter only, and never allowing workmen to come behind this. All orders should be signed by proper authority and a carbon copy of each transaction kept. Tools, in particular, and all stock that can be used about home, barn or garden will mysteriously leave the plant, a few cents worth at a time, if a way is found to handle the matter with an easy conscience.

SUMMARY

In the foregoing paper, I have attempted to point out to you

certain methods that can be adopted in the conduct of any manufacturing business. The days of large profits, cheap raw materials and labor have gone for good. With increasing prices and competition, all executives must be economists as well. Efficiency, in its broadest sense, should include promotion, capitalization, location, organization, equipment and operation. Great stress has been laid on the efficiency of labor to the exclusion of matters of equal or greater moment. An exact knowledge of unit costs will reveal the weak points in any plant. The so-called efficiency engineer who spends three or four days

in a concern and antagonizes everyone from the bosses to the office boy, can accomplish little good. Weeks and months of study are required to get at the details of the business; to make improvements is a still greater task. The good-will of the employees must be gained and kept to make any progress in economy studies. Discussion and argument naturally follow any change in policy. The man who makes the change should be on the ground to defend himself and drive home the facts as he sees them.

SYRACUSE, N. Y.

PERKIN MEDAL AWARD

The Perkin Medal was conferred on James Gayley for his distinguished services in the field of chemical engineering and metallurgy at the regular meeting of the Society of Chemical Industry, Chemists' Club, New York, January 24, 1913.

Mr. Gayley's study of the blast-furnace reactions covering a period of many years and his subsequent development, on the basis of these observations, of the dry-blast processes, as well as numerous other inventions in this field are fully set forth in the presentation address by Professor Charles F. Chandler and the address of acceptance by Mr. Gayley. Professor Henry M. Howe spoke on "The Value of Expert Opinion," particularly as applied to Mr. Gayley's work and Prof. Edward Hart gave a most interesting and intimate review of the career of the medalist. The program was completed by an address on "The New Age" by Dr. Rossiter W. Raymond.

At the conclusion of the program, the Society and its guests were entertained at an informal reception given by the Chemists' Club.

The addresses presented at this meeting are printed in full in the following pages. [EDITOR].

PRESENTATION ADDRESS

By C. F. CHANDLER

MR. CHAIRMAN, BLESSED CHEMISTS AND MR. GAYLEY:

It is my very pleasant privilege, as the senior Past-President of the Society of Chemical Industry, residing in this country, to present to Mr. James Gayley, the Perkin Gold Medal, for important achievements in Industrial Chemistry.

This medal has been awarded to Mr. Gayley by the Perkin Medal Committee of the Associated Chemical and Electrochemical Societies of America in recognition of his most valuable work in Chemical Metallurgy.

James Gayley is the maternal grand nephew of Sir Henry Bell, who established steam navigation on the Clyde, where he launched "*The Comet*" in 1812. He was born at Lock Haven, Pa., October 11, 1855, the son of Samuel A. and Agnes (Malcolm) Gayley.

He was educated at West Nottingham Academy, Md., and graduated from Lafayette College in 1876 with the degree of Mining Engineer. In 1906 he received from the University of Pennsylvania the Honorary degree of Doctor of Science, and in 1912 the same degree from Lehigh University. In 1908 he received the Elliot Cresson Gold Medal for the Promotion of the Mechanic arts from the Franklin Institute.

Mr. Gayley began his professional life as chemist for the Crane Iron Company, Catsauqua, Pa., 1877-'80. He was next superintendent of the Missouri Furnace Company, St. Louis, and later was the manager of Blast Furnaces, E. & G. Brooks Co., Birdsboro, Pa., 1880-'85. In 1885 he became manager of the Blast Furnaces at the Edgar Thomson Works, and he was subsequently promoted to the position of manager of the Edgar Thomson Works: he later became a managing director of the Carnegie Steel Company. In 1901, he was made first vice-president of the U. S. Steel Corporation, remaining in this posi-

tion until 1909. He was the inventor of furnace improvements, bronze cooling plates; stand for ladle in pouring Bessemer heats and the dry air blast.

Were it not that we have with us to-night Mr. Gayley himself, it would be my duty and pleasure to give you a history of his various most valuable contributions to metallurgical chemistry. But as you would certainly prefer to learn this from his own lips, I will content myself with saying that I can not recall a more far-reaching invention than that of the dry air blast for the manufacture of iron, for which he has received, between October 23, 1894 and September 5, 1911, no less than fifteen successive patents in this country. I am told that his results in this direction alone mean a reduction of from one-half to one dollar per ton in the cost of producing pig iron, besides making it possible for the iron master to produce, in all weathers, a product of uniform quality. When one remembers that there were produced in the United States, during the past year, twenty-nine millions of tons of pig iron, it will be seen that this, Mr. Gayley's invention of the dry air blast, means a saving to the American people of from \$15,000,000 to \$29,000,000 per annum.

I have presented to you very briefly the great achievements of Mr. Gayley in the field of Applied Chemistry, but quite fully enough to satisfy you that your Committee is fully justified in placing Mr. Gayley by the side of Sir William Perkin and the previous recipients of the Perkin Medal, as one of our greatest Industrial Chemists and Chemical Engineers.

TO MR. GAYLEY:

It gives me great pleasure, as the representative of the Society of Chemical Industry, and the affiliated Chemical and Electrochemical Societies, to place in your hands this beautiful token of the appreciation and affection of your fellow chemists.

ADDRESS OF ACCEPTANCE

By JAMES GAYLEY

MR. CHAIRMAN, LADIES AND GENTLEMEN:

I wish to thank the speaker for this medal which he has presented to me with such gracious words. I wish also to express my thanks to the awarding Committee and the societies which they represent in conferring this great honor upon me. I appreciate it still more because the Committee have stepped aside from what is purely the chemical industry to another great industry, that of metallurgy, which, nevertheless, is one in which the application of chemistry is the controlling factor, and this recognition of the broader field of chemistry brings with it a keen sense of appreciation of this rare honor and distinction conferred upon me. Again I thank you.

The iron blast furnace is but the chemist's crucible on a gigantic scale—operated on chemical principles and the mechanical appliances are instruments of precision, constructed and adjusted to carrying out in efficient manner the chemical reactions involved.

The "rule of thumb" practice, which ended thirty-five to forty years ago, is well-nigh forgotten—that period in which

chemistry was not applied, and a ton of ore was a ton of ore all the world over, irrespective of its reducibility or chemical composition; when the iron master was more interested in the output of 1.8 iron than in the fuel consumption, and would tell you that "lime made heat," and David Thomas, that grand old pioneer of the anthracite iron industry, summed up the requisites for successful furnace practice as "wind and heat." The application of chemistry to iron smelting has effected a wonderful transformation in that industry, so that to-day the chemist occupies the foreground in directing its operations.

Moisture in the atmosphere has long been recognized as a variable and influential element in the manufacture of iron. Truran, in his "Manufacture of Iron," written in 1862, refers at length to the influence of moisture on the quality and make of iron, and the increased consumption of fuel in the summer season, but does not touch on the problem of its regulation or removal.

Later, in England it was proposed to extract the moisture by passing the air over lumps of chloride of calcium, but Sir Lowthian Bell showed the impracticability of that scheme on account of the rapidly diminishing power of absorption possessed by the calcium chloride.

Charles Cochrane, an eminent iron manufacturer of Great Britain, proposed and obtained a patent on extracting moisture from the air by bringing it into intimate contact with liquid calcium chloride flowing over chains suspended in a chamber; but later he declared as to the benefits to be derived from extracting moisture that "the game was not worth the candle." Nevertheless, the moisture in the atmosphere was recognized as a disturbing element. Some of the earlier makers of anthracite iron in the Lehigh Valley stated that they frequently knew in the morning what kind of iron their furnaces were making by observing the weather conditions; yet, prior to the first dry air installation in 1904, this variable element of moisture was accepted in a spirit of resignation, as something to be endured, like storm and sunshine, a condition beyond control.

It was my privilege to be invited in 1885 to take charge of the Edgar Thomson Blast Furnaces of the Carnegie Steel Company, a plant which represented the most advanced construction in blast-furnace equipment, and was supplied with the best fuel and ores. In the operation of these large furnaces, the influence of the atmosphere was forcibly impressed, as the steel works were

being supplied with hot metal direct from the furnaces, for the Jones metal mixer had not come into use. It was a difficult matter to supply metal approximating uniformity even under the best conditions, and quite impossible under conditions of varying atmospheric humidity.

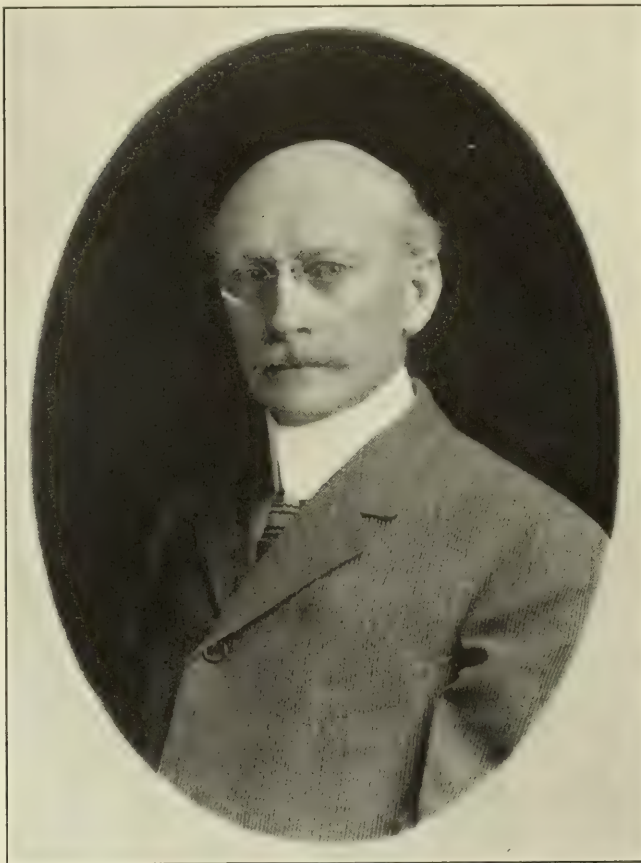
For several years observations were made twice a day of the moisture in the atmosphere, and a direct relation was established between the quantity of moisture and the grade of metal, with particular reference to the silicon which is the heat-producing element in the acid Bessemer converter. In the summer season, the air blown into the converter was heavily charged with moisture, and in consequence, a higher percentage of silicon in the metal was normally required, while at the same time these

atmospheric conditions operated on the furnaces to produce a lower silicon metal; thus the operating of furnaces in conjunction with Bessemer converters on direct metal may well be presumed to have been a difficult and trying proposition.

Under these conditions of manufacturing, the removal of the moisture from the atmosphere, or rather its reduction to a low degree, and one of practical uniformity, appeared to hold out the only means of effecting regularity, and at the same time to promise a considerable saving. It was a matter of constant observation that a sudden change in the weather, making a quick drop in the temperature and content of moisture, would cause the furnaces to work excessively hot, but this period of dryness could not be taken advantage of, for before any changes could be made effective in the furnace charge to meet current atmospheric conditions, the moisture might have increased to its normal seasonable amount.

Observations of the humidity in the atmosphere were made daily from 1886-1890, when the first experiments for moisture removal were begun. These observations were made, at the beginning, in the morning and evening, and later were made every hour. Observations were also made of rain storms, to determine the moisture before, during and after the rain, and it was noted that the moisture usually dropped quickly as the rain began to fall. Throughout this period of moisture tests, the working of the furnace was observed in its relation to the amount of moisture in the atmosphere.

A modern furnace consumes about 40,000 cu. ft. of air per minute, and for each grain of moisture per cubic foot, there en-



JAMES GAYLEY, PERKIN MEDALIST, 1913

ters the furnace one gallon of water per hour for each 1000 cu. ft., that is, if the moisture was 1 g. per cu. ft., 40 gallons of water would enter the furnace per hour.

TABLE 1—VARIATION OF MOISTURE IN THE PITTSBURGH DISTRICT

	Average temperature ° F.	Weight of water per cubic foot of air Grains	Water per hr. entering a furnace using 40,000 cu. ft. of air per min.
			Gallons
January.....	37.0	2.18	87.2
February.....	31.7	1.83	73.2
March.....	47.0	3.40	136.0
April.....	51.0	3.00	120.0
May.....	61.6	4.80	192.0
June.....	71.6	5.94	237.6
July.....	76.2	5.60	224.0
August.....	73.6	5.16	206.4
September.....	70.4	5.68	227.2
October.....	56.4	4.00	160.0
November.....	40.4	2.35	94.0
December.....	36.6	2.25	90.0

While the moisture in January averaged 2.18 grains, yet the total variation for the month was from 0.56 g. to 2.55 g., and while June shows an average of 5.94 gr., yet the extreme variation was from 4.8 g. to 8.50 g., or in other words the moisture entering the furnace varied from 192 to 340 gallons per hour. During the midwinter period, the moisture may vary as much as 150 per cent. in the same day, but in midsummer it rarely varies more than 25 per cent.

Having secured extensive data on the varying humidity of the atmosphere over a period of five years, the problem of making those conditions uniform next presented itself.

The experience of English engineers was against the absorption process with calcium chloride, and my predecessor at the Edgar Thomson Works, Mr. J. H. Cremer, had constructed an apparatus to desiccate in the same way, but he obtained very unsatisfactory results. As our observations showed a reduction of moisture through a reduction of atmospheric temperature, the reduction of temperature through mechanical refrigeration presented itself as the obvious method of removing the moisture, and on this basis the first experiment was undertaken in 1890 in a crude way.

We began by passing air through two chambers in succession; in the first chamber the air came in contact with pipes cooled by water, and in the second chamber anhydrous ammonia was expanded through the pipes. As the air came from the blowing engine it was quite warm, but after passing through the chambers it was very cold; each chamber was only six feet long and the volume of air treated was small indeed.

Various forms of apparatus were constructed from the period 1890-1895, and tests were made as opportunity offered. During this period my duties had been changed from that of superintendent of the furnaces to general superintendent of the whole works, thus adding to my duties that of the steel works and mills. There was in consequence not much time free to make experiments, for the demands of a large steel works on its manager's time were persistent and exacting, and experiments and improvements along other well defined lines represented more immediate profit and demanded thought and attention. But the general plan for a final test on a large scale had been worked out, which was to be tried later. In 1896, I left the active management of the works to enter upon the general business of the Carnegie Steel Company in connection with the ore department and the assembling of all raw materials. If the opportunities for experimenting were rare when stationed at the works, they became more so, when located in the general office.

I therefore secured the services of a young engineer, Mr. Walter, from a refrigerating company, and when they learned

the nature of my experiments they kindly loaned me a small ammonia compressor to carry on the work, and we used two air drying chambers—each four feet square and eight feet long, and filled with pipe coils, and with the necessary refrigerating appliances. A blast engine with an air cylinder three feet in diameter and capable of supplying 3500 cu. ft. of air per minute was installed, and from this engine and its small air supply the data were worked out for treating 40,000 cu. ft. of air, which was the quantity required to supply a modern blast furnace.

I mention that we had to work out the necessary data for a practical demonstration, and the suggestion might arise, why did we not avail ourselves of the experience of refrigerating firms? Indeed we tried to—the proposition was put up to several important makers of refrigerating machinery, but without any substantial benefit. To refrigerate the air for cold storage rooms was a specification they readily understood, but the treating of a hurricane of air was an entirely different problem to them. We were therefore compelled to work out the data ourselves and make out our own card of estimate.

It is unnecessary to give in detail the many and varied experiments made in treating the air, nor to describe how certain obstacles, which seemed to block our progress, were successively overcome. In our list of experiments we tried rarefaction with refrigeration but we did not obtain satisfactory results.

About the year 1900, we had plans worked out in detail for a plant to treat 40,000 cu. ft. of air per minute, and I then applied to my company for an appropriation of \$100,000.00 to make this installation; here my most difficult work began—to persuade my associates that air really did carry moisture and that it could appreciably, even in a small degree, affect the working of a blast furnace.

It could hardly be expected that men who came up through the ranks of the steel works or office could appreciate the influence of atmospheric changes on a blast furnace that to all external appearances was crude and rough, but which in its interior adjustment was really on a most delicate balance. Money was readily appropriated for the mechanical appliances of the furnaces, or for securing uniformity in the physical and chemical composition of the ores, coke and limestone, and a variation therein of 10 per cent. to 20 per cent. was promptly corrected, but the atmosphere might vary from 20 per cent. to 150 per cent. even in a single day, without giving any concern, for few realized that the weight of air consumed per ton of iron was 50 per cent. greater than all the other raw materials combined. In other words, it requires about four tons of ore, coke and limestone to make a ton of pig-iron, while six tons of air are required.

The most difficult problem I had to encounter was to convince others of the merit of the process after its details of construction and operation had been worked out, and it was not until 1903 that I secured an appropriation to construct the first plant, although I had offered the year before to assume personally half the expense.

Early in June, 1904, the dry air plant, which was erected at the Isabella Furnaces at Pittsburgh, was in proper working order and ready to be put on the furnace. It was necessary to apply the dry air gradually so as not to disturb the furnace adjustment, and as there were three blast engines we arranged to first supply dry air from one engine, making the blast one-third dry air. We decided to apply this dry air at 9.00 A.M., and I had the weight of ore charge increased by 5 per cent., and this increase was timed to reach the combustion zone of the furnace at 11.00 A.M. The furnace manager regarded with dismay the addition of 5 per cent., protesting that a 2 per cent. increase was about the limit, and if the dry air did not prove efficient, then he would have a very cold furnace on his hands. Notwithstanding, the change was made. When the dry air was turned on at 9.00 A.M., the furnace soon showed the effect

of it, the gas became grayer, a sure sign of the furnace working hotter, and when the 5 per cent. increase in ore had reached the hearth, it was not discernible that the furnace had been given an increased duty.

The operations of the furnace were conducted on a conservative basis, and the long time spent in working out and developing the air drying plant was rewarded, for the plant started and continued to perform its work without a hitch. By the sixth day the furnace was being supplied with two-thirds dry air and one-third natural air, and 9 per cent. increase in ore charge had come to work, the furnace continuing splendidly. I might add here that the 9 per cent. in weight of ore charge represented the same percentage increase in output, and a like reduction in the amount of fuel used per ton of iron.

On the afternoon of that sixth day in the use of dry air, I left the works, well satisfied with the progress made, and confident of the future by reason of the many little indications easily recognized by practical furnacemen, that a still heavier duty would be responded to.

I had not gone far when the sound of an explosion reached me, and, on turning, I saw great clouds of steam rising from the works. I hastened back, and feeling my way through steam and dust, I was dismayed to find that the refrigerating chamber had collapsed. There it lay a tangled mass of concrete and distorted pipe coils.

During a part of the time employed in erecting the dry air plant there was a bricklayers' strike, and the works manager, not wishing to delay construction, built the refrigerating chamber of concrete. The dry air blast conduit leading from the top of the chamber to the blast engines was constantly vibrating from the impulse of air and the vibrations of the engines. These were in turn communicated to the dome of the building, weakening the bond of the concrete; this caused the walls to collapse; in their fall they broke the steam pipe leading to the compressors. The debris was cleared away, and in less than two months the plant was again started. We began as before, and in two weeks' time had secured a fuel economy of 15 per cent., and then by small increments we gradually worked up to a point of 20 per cent. efficiency; that is, we effected a fuel saving of 20 per cent. and increased the output to the same extent. This practice was continued for about six months, but it was operating too close to the danger line to take care of irregularities in the raw materials, and the fuel economy was adjusted to 15 per cent. Even with dry air blast there is a disinclination to work up to the high limit of efficiency, for the experience of every furnace manager with natural air has shown the necessity of keeping a good margin of safety.

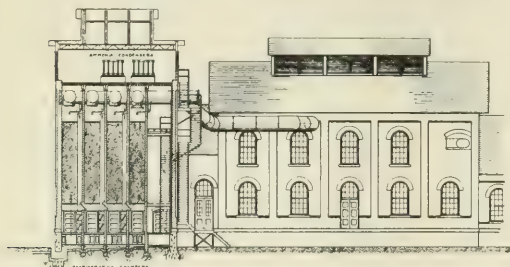


FIG. 1—SECTION OF REFRIGERATING CHAMBERS AND ELEVATION OF BLOWING ENGINE HOUSE

The apparatus for drying air is shown in the two models presented. In the first model, which represents our first installation, there is a chamber filled with pipes, and the air is cooled by indirect contact with cooling fluid, which is brine. The temperature of the brine is such that the air entering the chamber at 80° is discharged at 23°.

The second model represents a two-stage process, in which the air is brought into direct contact with refrigerated water in the first chamber, and is reduced to about 35°; then passes

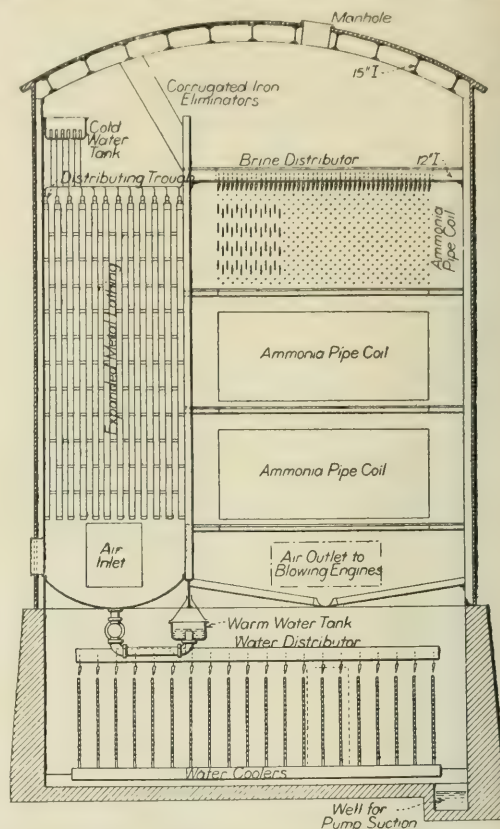


FIG. 2—TWO-STAGE REFRIGERATING CHAMBER. COOLING BY DIRECT AND INDIRECT CONTACT

to the second chamber filled with pipe coils through which brine circulates and the final temperature is obtained. The two-stage method is more cheaply operated, and costs a third less to build.

It was not our purpose throughout our experiments to work

TABLE II.—GALLONS OF WATER DELIVERED TO FURNACE IN 24 HOURS

	Natural air	Dry blast		Natural air	Dry blast
July, 1910			July, 1910		
1.....	5,349	834	17.....	4,116	809
2.....	5,517	849	18.....	3,588	809
3.....	5,438	829	19.....	3,410	809
4.....	4,432	814	20.....	3,915	819
5.....	5,488	844	21.....	6,119	809
6.....	7,797	849	22.....	4,678	814
7.....	5,428	844	23.....	5,876	814
8.....	5,873	799	24.....	6,327	834
9.....	6,633	829	25.....	5,152	819
10.....	5,981	819	26.....	6,450	829
11.....	4,511	785	27.....	5,764	809
12.....	6,203	804	28.....	5,453	809
13.....	4,002	779	29.....	6,184	819
14.....	4,713	785	30.....	4,525	799
15.....	5,828	809	31.....	4,288	782
16.....	5,522	819			
Total, July.....				164,560	25,254
Equivalent in barrels of 42 gal. each.....				3,918	601

out the most economical method of drying air for the first installation. What we aimed at was to construct a plant that

would efficiently and continuously produce dry air, in order to determine its economical value in the furnace.

Fig. 3 shows the variability of moisture in natural air, and the regularity of dry air in the month of July, 1910. Table II shows the meaning of the curves in Fig. 3 when translated into terms of gallons and barrels of water.

The quantity of water extracted in July, if placed in barrels, would make a row of barrels about one and one-half miles long.

The records obtained at several works from the use of dry air, and which in each case cover a considerable period, are as follows:

Works	A	B	C	D
Output, percentage increase.....	23.0	15.3	11.8	16.0
Coke used, percentage decrease....	10.5	6.0	9.8	10.5

The results obtained at different plants are modified by the raw materials used and the personal equation of the management enters into it. The results given above are taken from works in three different countries. *The claim I personally make for the process is that with an increase in output of 10 per cent., the saving in fuel per ton of iron will be reduced 10 per cent., and I consider this conservative.*

that the furnace works with greater regularity and, in consequence, a more uniform metal is produced, and a required grade of metal can be made with precision.

In low-silicon irons the sulfur does not increase as when natural air is used.

The saving in coke effects a corresponding saving in the limestone necessary to flux the ash of the coke, and there is less phosphorus entering the metal.

As the furnace charges settle more regularly, there is less fine ore carried over with the gases.

A manager of blast furnaces using dry air recently said that they found it to be an "educator" in their practice, as it had taught them the advantage of securing regularity in many other directions.

I shall not attempt herein to set forth any of the theories advanced to account for the fuel saving, which has been found to be in excess of what is necessary to dissociate the moisture. That feature has been ably discussed by Dr. Henry M. Howe, Dr. R. W. Raymond, Prof. J. W. Richards, Mr. J. E. Johnson, Jr., and many others in this country, and also by metallurgists

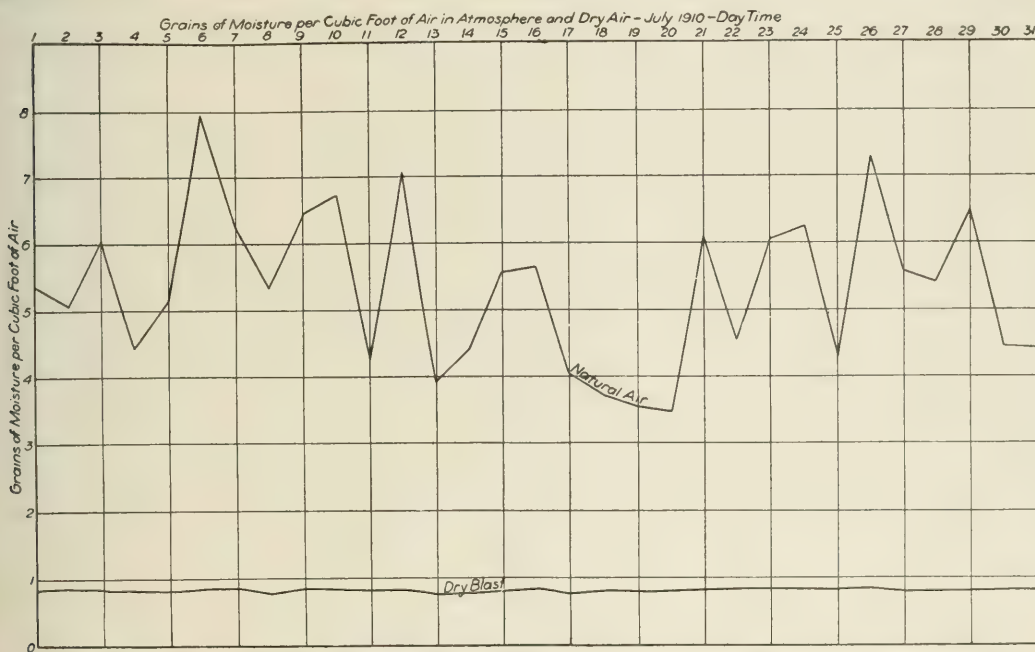


FIG. 3.—RESULTS WITH THE GAYLEY DRY BLAST. GRAPHIC CHART OF THE PERFORMANCE OF A WESTERN DRY-BLAST PLANT

One of the advantages obtained through dry air is the elasticity it permits in furnace operations to meet business conditions. If trade is dull the furnace can be operated to secure the maximum of fuel economy with a small increase in output, but when trade is booming and pig iron is in demand, an increased output is more desirable than a saving in fuel, and the furnace can readily be made to respond.

The manager of the Dowlais Works, at Cardiff, Wales, experimented with one furnace to determine what results could be obtained under each condition of operating.

For a period, the furnace was operated principally to secure increased output and obtained an increase of 26 per cent. with a fuel saving of 12.3 per cent.

In the next period they operated principally to obtain decreased fuel consumption and obtained an increase in output of 12 per cent. with a decrease in fuel of 17.4 per cent.

In addition to the advantages already mentioned, it is found

in England, Germany, and France; their full discussions can be found in the *Transactions of the American Institute of Mining Engineers*, the *Journal of the British Iron and Steel Institute*, and metallurgical journals.

Towards a full consideration of the dry air blast, a few points may be briefly referred to.

It did not come into its work as did the Neilson hot blast in 1828, when the art was crude, and the appliances of the furnace were poorly adapted to the work. But to the Scotchman, Neilson, all credit is due for effecting a fuel saving of thirty per cent.

Dry air instead was tried out when the equipment of the furnace was as perfect as human skill could make it. The nature of furnace operations was well understood, and its management was on a skilful and scientific basis.

Nor was it possible for dry air blast to have an experimental stage. Nearly every device or process can be tested in an experimental way, and on a comparatively inexpensive scale.

Bessemer could blow air through molten metal in a pot and demonstrate the value of the pneumatic process, but it would have been of no value to build a small plant to refrigerate a part of the air; nothing conclusive would have been gained. Nor would it have been of any value to treat the whole air supply of a diminutive or toy furnace. To efficiently demonstrate its value, it had to be applied to a furnace that was equipped and operated according to the most advanced state of the art, and not only was it essential that the whole air supply should be treated, but that the method and means of treatment should measure up in capacity and efficiency, and operate as continuously as any of the other accessories of a modern blast furnace.

This, in brief, is the story of the dry air blast.

THE VALUE OF EXPERT OPINIONS¹

By HENRY M. HOWE

Interesting as are the other aspects of the Gayley process its greatest interest lies, I think, in the light which it throws on the nature of expert evidence and on the value of expert opinion.

What is this process? It is simply drying the air used for burning the fuel in the iron blast furnace—apparently a rather simple matter. To refresh your memory, the blast furnace is a huge vertical firebrick cylinder, roughly speaking. In it iron ore, which is essentially iron oxide, is converted into cast iron or pig iron by prolonged exposure to coke or its equivalent, in an atmosphere of mixed carbonic oxide, carbonic acid, and nitrogen, which results from burning this coke by means of atmospheric air forced in through appropriate openings near the bottom of the furnace, and called "the blast." The furnace is full from top to bottom of an intimate mixture of this coke and ore, together with limestone added for the purpose of forming with the barren mineral matter of the ore and with the ash of the coke a fusible silicate or slag, and for other purposes into which we need not enter here. These three solid materials collectively are called "the stock."

The burning of the coke generates at the bottom of the furnace a temperature so high as to melt away the bottom of this column of stock, or mixed coke ore and limestone, of which the last two have, by this time, been converted locally into metallic iron and lime, and as the column thus descends it is renewed at its top by adding more of this same mixture so as to keep the furnace continuously full.

There are, as it were, two rivers passing through this great cylinder in opposite directions, a sluggish river of solid stock which descends as its bottom is melted away, and a swift river of ascending gases resulting from the burning of the coke by the injected air or blast. The former traverses the length of the furnace in from 12 to 15 hours, the latter in a very few seconds. These rivers interact as they interpenetrate and flow past each other, the rising gaseous column progressively giving up its heat to the solid column and taking from that solid column the oxygen of its iron oxide, so that the gaseous stream as it emerges from the top of the furnace has taken from the descending ore all the oxygen that it is capable of removing, and has delivered over to that ore and its accompanying coke and limestone all the heat that they are capable of taking from it.

So much for the blast-furnace process, which, like every mundane process that seems simple, is in fact of a complexity so overwhelming that the human mind is inherently and incurably impotent to grasp it. We rub our eyes and, seeing as far as the ends of our noses, assume that we see to the end of the universe.

As a heat engine the blast furnace was known to be extremely efficient, as human heat engines go. Nevertheless, by the

extremely simple step of drying the blast Mr. Gayley made a further important saving of fuel amounting in some cases to 20 per cent., and according to our present evidences to about 10 per cent. on an average, for usual American conditions. To those who had taken up the logical stick by the wrong end, such a saving by thus drying the blast seemed simply preposterous, as preposterous as talking a thousand miles through an iron wire, or waving a message to Europe without any wire, or as any invention is till you understand it.

Its preposterousness was promptly and convincingly exposed by the public-spirited experts whose geographical misfortune prevented their knowing Mr. Gayley's character, though those of us more favored geographically followed "Br'er Fox" till our question "Why and how?" could be answered.

The heat required for heating and dissociating the moisture of the blast is a small fraction of the total heat requirement of the blast-furnace process; how then dare we say that the removal of this heat requirement may save 10 or even 20 per cent. of the fuel?

Not a few of us had grown so used to calculating the heat needed for a given chemical and physical work like that of the blast furnace, and the heat evolved by the combustion of a given weight of fuel under known conditions, and to calculating thus the thermal balance, that we had lost sight of the supreme importance of temperature.

The atmospheric moisture, calorimetrically considered, is indeed slight, but thermometrically considered it is sometimes of overwhelming importance. As to its effect on climate Tyndall says: "To say that on a day of average humidity in England, the atmospheric vapor exerts 100 times the action of the air itself, would certainly be an under-statement of the fact."

Those who have felt the physical and mental exhilaration which a ten-mile trip from Cairo out into the desert creates by the sudden substitution of a drier for a moister climate; those whose legs would fain leap when the "wild west wind, thou breath of Autumn's being" suddenly dries our air, might well listen to the claim that a like drying of the air affects the blast-furnace process as it affects our own vital processes.

The sum and substance of it is that the blast-furnace process has, among its various duties, to supply a certain quantity of heat at or above a certain high temperature, which for brevity we may call the critical temperature, while shamefacedly confessing that we are further overworking an already grossly overworked word. No quantity of heat offered at any lower temperature will do this work. All the heat in all the suns of the milky way if offered at a temperature of 50° C., could not boil one egg.

Drying the blast saves fuel by improving the temperature-distribution of the heat generated.

Perhaps this is more readily understood if we consider an imaginary case. Suppose that matters were so ordained that he who wished to build an iron building was obliged to take, along with his iron work, a certain fixed proportion of accessories, windows, flooring, tiling, etc., the proportion fitted for a ten-story building. That would be all well enough for those who build nine- ten- or eleven-story buildings; but for the builder of a forty-story building it would be most uneconomical, because whereas the quantity of accessories, windows, flooring, tiling, etc., increases directly as the height of the building, the iron work needed increases in a higher ratio; so that, in order to get enough iron work for his forty-story building he might have to get enough accessories for a sixty-story building, and the excess would be left on his hands. This is because of bad proportioning of his supplies. A mere change in the proportion between iron work and accessories would cause a great saving.

It is somewhat so with a thermal process like that of the iron blast furnace. When combustion has raised the temperature above the critical point there is available first a certain

¹ Address delivered at the Perkin Medal Meeting, Society of Chemical Industry, Chemists' Club, New York, January 24, 1913.

quantity of heat above that temperature, the hyper-critical heat, and second another and larger quantity of heat below that temperature, the hypo-critical heat, the heat remaining when the temperature has sunk to the critical point. The hyper-critical heat is needed for certain work which can be done only at hyper-critical temperatures, the hypo-critical heat is available for work which can be done at hypo-critical temperatures; so that, just as we have hyper- and hypo-critical heat, so we have also hyper- and hypo-critical work.

FOR HEAT ECONOMY THE HYPER-CRITICAL HEAT SHOULD BE TO THE HYPO-CRITICAL AT LEAST AS THE HYPER-CRITICAL WORK IS TO THE HYPO-CRITICAL WORK. The proportion between the two evidently depends on the temperature reached by combustion itself. The higher this temperature, the higher proportion does the hyper-critical heat bear to the hypo-critical heat.

If the temperature developed by combustion is so low that the ratio of hyper- to hypo-critical heat is too low, is below the ratio of hyper- to hypo-critical work, then in generating enough hyper-critical heat to do the hyper-critical work we are forced to generate an excess of hypo-critical heat over and above the hypo-critical needs of the process, and this excess of hypo-critical heat is used to poor advantage or is wasted. If my ratio of iron work to accessories is too low, then in providing my building with enough iron work for forty stories I am forced to provide enough of these accessories for sixty stories, and the excess is left on my hands. And as a mere change in the ratio between iron work and accessories can enrich or ruin a builder, so a mere change in the ratio between hyper- and hypo-critical heat, induced by a change in combustion temperature, can lead to a wholly disproportionate change in the economy of our own vital processes or of the process of the blast furnace.

Thus it was with Neilson's introduction of the hot blast. Formerly blast furnaces were fed with cold air, with the result that, because of the low temperature of combustion, the proportion of hyper-critical to hypo-critical heat was far below the proportion of hyper- to hypo-critical work needing to be done, with the result that the burning of enough fuel to provide enough hyper-critical heat yielded a quantity of hypo-critical heat far in excess of the hypo-critical work to be done, and this excess was used to poor advantage or wasted. Hence raising the temperature of combustion by heating the blast led to a saving of fuel which, to those unable to think, was miraculous.

The degree of economy caused by blast-drying should vary from case to case with the initial lack of hyper-criticalness in the combustion temperature; and if there is no such lack initially, as may happen conceivably, then blast-drying should cause no economy.

Other means of adjusting the ratio of hyper- to hypo-critical heat suggest themselves, such as raising the temperature of combustion by further preheating the blast, by enriching it in oxygen, by removing part of the atmospheric nitrogen, or by electric induction at the very focus where the hyper-critical work goes on; and lowering the critical temperature by changes in the conduct of the process. We have not reached the end of knowledge in general, or of the improvement of the blast furnace process in particular. But the fact that blast-drying, in removing the effects of the fluctuations in the atmospheric moisture removes a serious cause of irregularity in the working of the furnace and in the quality of its product, gives it an administrative and commercial advantage over other means of raising the combustion temperature which may well be decisive.

The explanation which I have given you is not my own, and it may not be the only one or even the chief one. It is the only reasonable one which I have heard of the accomplished fact which it aims to explain, and it seems to me adequate.

The total quantity of pig iron made in the world in one year is some sixty-six million tons, consuming somewhere about sixty-six million tons of coke and its equivalents, and this in

turn represents about ninety-five million tons of coal. A 10 per cent. saving of fuel if applied to all the blast furnaces in the world would represent a saving of some nine and a half million tons of coal a year, or more than 40 per cent. of the coal production of so important a coal country as Belgium.

The scale is a large one. In how many of these furnaces such a saving can be made remains to be proved, but the results already reached lead us to expect that the total saving will be of very great importance.

The deliberation and caution, indeed the tardiness with which the iron trade has proceeded in adopting dry blast is referable to various reasons, such as hesitation to incur the certainly great expense of its installation, the competition of other devices for increasing earnings in other directions, the wish of each to get the benefit of the experience gained by its earlier adopters, uncertainty as to whether the saving found by John Doe will apply to the different conditions of Richard Roe's furnace, and the like.

But after all is said and done, that which interests us most is not the invention itself, important as that is, nor the great saving of fuel. The striking thing is the contrast between the mental attitude of the certainly very learned men of science who immediately stamped Mr. Gayley's claims as preposterous, and the attitude of this great captain of industry, who not only saw the saving to be effected but saw it so clearly that he was able to bring to pass the very costly experiments needed to prove his faith. Let us learn the lesson of humility. Natural human caution is likely to prevent the cautious from saying "I know that so and so can be done" unless they do know it; but such cases as this show that it does not prevent even the well qualified, the expert, and the prudent, from saying "So and so can not be done," though in fact it ought to prevent them, in view of the almost infinite excess of our ignorance over our knowledge.

DR. GAYLEY'S INTEREST IN EDUCATION¹

By EDWARD HART

This is the second time I have participated in rejoicings in Dr. Gayley's honor. The first festival was held early in 1902, when we dedicated Gayley Hall to chemistry and metallurgy at Lafayette College. Then, too, Dr. Howe spoke, and many of those I see here to-night were present. Dr. Thomas M. Drown, Dr. Gayley's preceptor and mine, greatly beloved, now gone to the far-away country, spoke, and Dr. Ira Remsen. It was a great celebration. One of the college boys told me that never before had so many high hats been seen on that campus.

We dedicated then a new library as well—The Henry W. Oliver Chemical and Metallurgical Library of Lafayette College, endowed by Mr. Henry W. Oliver, one of Dr. Gayley's associates, long engaged in the iron and steel business. This gift was made at Mr. Gayley's suggestion.

Dr. Gayley is a working trustee of Lafayette College. He has given time and money to the College, not once, but many times. One of his recent tasks has been the erection of a new building for the Department of Mechanical Engineering. I have often been struck with the originality and keen intuition, which he shows here as elsewhere. One of his ideas is compulsory athletics for all students.

I went to Lafayette College in 1874 with Dr. Drown, as his assistant. I was nineteen years old and had never seen the inside of a college building. Gayley was then a junior and probably knew more about chemistry than I did. In his senior year I was in charge, during Dr. Drown's absences, of the quantitative laboratory where Gayley was working. I was never, therefore, in any proper sense Dr. Gayley's teacher.

Gayley is the son of a Presbyterian minister, not blessed with great wealth; like many poor boys he received help from

¹ Address delivered at the Perkin Medal Meeting, Society of Chemical Industry, Chemists' Club, New York, January 24, 1913.

the college funds. He was not much of a talker then, but had a keen sense of humor. At that time F. H. Daniels, of Worcester, Mass., was also an assistant in the laboratory. The boys called him *Asenic*, because that was the way he pronounced it. Daniels and I undertook to listen to the different preachers, and one Sunday evening visited the Presbyterian Church in Phillipsburg. Gayley and his friend Peacock were there too, and next morning we were accused of slipping over to P-burg on the sly to see the girls. What they were doing did not appear.

When he left college, Gayley became chemist for the Crane Iron Co. at Catsauqua. At that time a chemist was considered an ornament rather than a necessity, and his value was greatly increased if he were of economical habits. Mr. Frank Horn, of Catsauqua, thinks his salary was \$35 a month at the start and there is a tradition at Catsauqua that the Directors of the Crane Iron Co., upon one occasion, gravely discussed Mr. Gayley's petition that his compensation be increased from \$40 to \$45 and finally concluded that the additional expense was not warranted. The books of the company show that he was paid at the rate of \$500 a year in 1879. They also show that Mr. H. J. Seaman, who succeeded him, at one time received as much as \$100 a month. Perhaps this was the belated result of Gayley's persuasive work with the Directors.

Everyone who knew Jim Gayley at Catsauqua remembers him pleasantly. He likes to go back there where everyone calls him "Jim." While there he lectured on chemistry in the Presbyterian church and afterwards appeared as one of the "babes in the wood" in a church entertainment. I venture to predict that if Dr. Gayley ever has a return engagement in either of these rôles, no building in the Lehigh Valley will contain his audience.

While in Catsauqua he lived at the hotel kept by Captain Harte. He still holds in affectionate remembrance the pies Mrs. Harte used to bake. I can remember that when he came back to visit us at the college he told us that it cost less to run his laboratory than any other in the Lehigh Valley.

The major part of the education we receive is self-education. Some men have never had much beside self-education. When I remember what Mr. Gayley was then and see what he is now, I am thoroughly convinced of the fineness of his fiber. Every time I met him he showed evidence of improvement—of the working of that yeast with which only the great are infected.

After leaving college he often came back to commencement, and I saw him once or twice in Pittsburgh. I had been plugging away at chemistry in Jenks Hall, which was the chemical laboratory from about 1881 to 1902. I taught descriptive chemistry, analytical chemistry, organic chemistry, theoretical chemistry, chemical technology, assaying, blowpiping, metallurgy and scientific German. During the intervals I worked for a living. Our laboratory was poorly equipped and I was very short of books. One day Mr. Gayley came in and after some general talk suggested that I get up plans for a new laboratory. I had heard that sort of suggestion before from others and nothing had come of it. So I acquiesced, but did nothing. Some months afterward Mr. Gayley again suggested that I get up plans and said that he would pay for them. I consulted the President who told me that Gayley had made a lot of money and that he was probably in earnest. Then I consulted an architect and in a short time Gayley Hall was in full blast. Imagine my feelings. For 20 years I had labored with my college work as one almost without hope, when suddenly all my wishes were fulfilled and I found myself with a handsome, well-equipped laboratory, an endowed library and assistants enough to enable me to do really good work. I must leave some things unexpressed. I cannot possibly express my feeling for Dr. Gayley. On the return trip to New York, after the dedication of Gayley Hall, Dr. Drown, then president of Lehigh

University, was one of the party, and Mr. Gayley offered him \$5000 for the University, which Dr. Drown accepted. This was used by Dr. Drown as a part of the fund for the erection and equipment of a Mechanical Laboratory at Lehigh. I think this gift was prompted more by his love for Dr. Drown than for any other reason. Lafayette and Lehigh are athletic rivals and it is necessary for Lafayette men to practice a certain amount of discretion in confessing fondness for Lehigh. If Mr. Gayley is to be convicted of love for Lehigh, he must himself confess it. I know, however, that many Lehigh men are fond of him, for Dr. Drinker is my authority; the best evidence of this is the honorary degree which Lehigh gave him last June.

About this time Mr. Gayley gave \$5000 to Dr. J. A. Brashear, of the Allegheny Observatory. This gift may also have been a personal one, prompted by the love which Mr. Gayley felt for him: a feeling shared by all Brashear's acquaintances.

Sometimes Gayley was willing to educate the older generation. There is a story going the rounds, unverified, that shortly after he assumed charge at Birdsboro, the furnace began to give trouble. Of course, Mr. Brooke was greatly interested and asked many questions. Finally Gayley could endure this no longer. He told Brooke not to bother any more, the furnace would come around all right and when it did he would send for him.

My friend, Dr. J. W. Richards, says that he once asked Gayley what his calculations showed in calories with dry air as compared with natural air. Gayley replied that he didn't know nor give a whoop about the calories; what he was interested in was the pounds of coke saved per ton of iron.

When Gayley Hall was about completed he came over from New York to look at it. I found him standing out in the quadrangle looking up. "That's a fine building," he said. Then we went in and stopped a moment in the hallway. "My! that's a fine building," said Gayley. When we went into a laboratory, plain, unadorned, modeled after the laboratory of a steel works; "By God, that's a fine laboratory," said Gayley.

I have had the good fortune to know a good many men whom I consider really great men—and by the way, have you ever noticed how prolific our country is of such men? Most of them are, of course, chemists. Without being invidious, I may mention such shining examples as Dr. Drown, Dr. Raymond, Dr. Howe, Dr. Chandler, Dr. Nichols, Dr. Morley, Dr. Acheson, Dr. Remsen, Dr. Wiley, Dr. Smith of the University of Pennsylvania—one must particularize when speaking of Smiths—and Dr. Loeb, just departed, and I have noticed one characteristic common to them all—very prominent in all of them. I mean their great consideration for other folks' feelings. Mr. Gayley belongs in this class. When pleased he expresses himself fully, when not pleased—silence. Consideration for others is so natural to Jim Gayley that I don't believe he half realizes what a good fellow he is.

In essentials he seems to me very like my dear friend and preceptor Tommy Drown, whom, as his assistant for many years, I knew well. Surely, I may praise the dead whom I loved and whose memory is dear; sympathetic in all that was good and true, aspiring, just—no, generous, always fair, carefully concealing a heart of pure gold. It is a privilege to have associated with such men.

Mr. Harold Chidsey, who is one of the instructors at the Tome School for Boys at Port Deposit, Maryland, speaks in the warmest terms of Mr. Gayley's work there. In Mr. Chidsey's words, "He is a live trustee." I am quite sure this is true, for Dr. Gayley has often spoken to me about the school; about their high ideals and the wonderful work they were doing. He was particularly anxious that at Lafayette our work should be of the same high order.

What may we not hope to accomplish at Lafayette College with such leadership? I confess to the belief in a great future.

Away from the hurricanes which rage in the cañons of lower Manhattan, the effete civilization of Wall street, and the lures of Broadway, we must endeavor to build up a sacred city dedicated to the purity of truth.

THE NEW AGE¹

By ROSSITER W. RAYMOND

There is no possibility of denying that we live in a new age. I know that this has been said, and I suspect that it has been true, of every age since Lamech handed the administration over to Tubal Cain; but that does not prevent its being true to-day—more truly true than anything previously declared, because it is true for us. People do not agree as to the exact particulars of this novelty, or their exact value, or the spirit in which they are to be received. Enthusiastic voices of youth, shouting the war-cry "Whatever is, is wrong!" rejoice in every change as a step of victorious progress. Deprecatory voices of age declare that they recognize, in many of these changes, old errors, which, once exposed by experience and killed after long struggle, are not entitled to a resurrection; and that progress backwards is not real progress at all. Yet, after all, for good or evil or (as usual) both, it is a new age. Let us see whether we cannot point out some features in it, concerning which all parties can agree. Before engaging in this perilous attempt, permit me to remind you of the universal proposition that science is quantitative. No enumeration of facts, causes and factors can constitute a science until it begins, at least, to weigh and measure them, and to determine their relative effect and importance. It is for this reason that political science, as a body of laws deduced from established facts, and universally accepted by competent investigators, does not yet exist. It presents, in lieu of well established facts, ardent assertions, supported by statistics, more or less carefully compiled, and more or less intelligently interpreted; and the laws of a science cannot be derived by induction from such inexact and disputable data, to which, even if they be unassailably true, no relative value has been quantitatively assigned.

In the absence of the means of such scientific induction, there is sometimes at command a short method, which roughly checks the conflicting claims of theorists and reformers. The Egyptian King, when his engineers differed violently as to the grade of an irrigating ditch—each party producing the notes of its survey to support its assertion—turned water into the ditch, and decided the question-at-issue by observing which way the water ran. In like manner, when we are shown conclusively that the conditions of labor in this country are worse than in other lands, we look at the statistics of immigration, and finding a mighty current, running only one way, we form our general working hypothesis accordingly.

It is by this method that I ask you to consider our new age, as indicated not in this country alone, but throughout the civilized world, and to recognize certain world-wide facts.

1. In the first place, the old world, after many centuries, during which it barely succeeded in feeding and clothing itself, is at last growing rich. Up to, say, fifty years ago, how beggarly was the surplus—a few hundred palaces, a few thousand pictures and statues, a few millions of accumulated gold, silver and jewels. In these respects, fifty years of to-day are more than a cycle of yesterday.

2. What has been the chief cause of this change? Not government, not commerce, not war, not social reform, except so far as these contribute to the fundamental condition. For the phenomenon is the ability of the world to feed and clothe and shelter its population, and still have labor to spare for industries not directly productive; and the cause must be the greater productivity of the individual man.

3. This has been achieved, first, by increasing the equipment of the man by means of knowledge, and then by his use of that knowledge in summoning and controlling the powers of nature, to reinforce his own. In short, applied science, under and before all other causes, has transformed human life.

In connection with the first point—the increase of individual knowledge, permit me to repeat a statement, uttered by me ten years ago, in an address on the Dynamics and Ethics of Engineering. It is so delightful to be able to reiterate without change an opinion ten years old!

"What is Engineering? The control of nature by man. Its motto is the primal one—'Replenish the earth and subdue it'—not merely depend upon it, like a stationary plant or roaming beast, or hunting savage, taking what it gives—but change it by creative work, and use it with sovereign skill. Is there a barren desert—irrigate it; is there a mountain barrier—pierce it; is there a rushing torrent—harness it. Bridge the rivers; sail the seas; apply the force by which all things fall, so that it shall *lift* things. Recover the solar energy long stored in black darkness to reinforce the sunshine of to-day with heat and light and power. Nay, be 'more than conqueror,' as he is more who does not merely slay or capture, but makes loyal allies of those whom he has overcome! Appropriate, annex, absorb, the powers of physical nature into human nature!

"In the execution of this primal command, the use of machinery has been the factor and measure of progress. It is a truism of to-day that the most civilized nation is the one which uses the most coal. Probably that will not always remain as accurate a test as now. Regions which have no coal may come to utilize water power, and its transmission by means of the electric current, so as to realize something of the benefits of modern engineering. So I will not say that it will always be the country that uses the most coal, but I think it will always be true that the nation which is foremost in the utilization of some natural power will be also foremost in every branch of human progress.

"For what is the species which we seek to perpetuate? Not an animal form merely, which can eat, fight or hide, or run away, nurse children, and die. No! the species is *progressive* man, linked in his origin with the grass and the beast, but in his destiny with the universe and its Creator.

"For we have to consider now not merely the descent, but also the ascent of man—a nobler evolution, which I have attempted to describe in modest verse.

THE ASCENT OF MAN

He stood upon the earth, and turned
To gaze on sky and land and sea,
While in his ear the whisper burned,
'Behold, these all belong to thee!'

O wondrous call to conquests new!
O thrill of blood! O joy of soul!
O peaks with ever-widening view!
O race, with still-receding goal!

He heard; he followed, evermore
Stumbling and falling, wandering far,
Yet still advancing, while before
His footsteps shone the guiding star.

He cleft the seas; the torrent loud
He harnessed to his need or whim;
He bade the lightning of the cloud
Run with his words, and toil for him.

He pierced the rock; he scaled the steep;
Destroyed; created; brought to light
The secrets of the deepest deep,
The glories of the highest height!

¹ Address delivered at the Perkin Medal Meeting, Society of Chemical Industry, Chemists' Club, New York, January 24, 1913.

The Future and the Past he scanned,
 With sense refined and vision keen,
 Explored, beyond this lower land,
 The treasures of a realm unseen.

Until he stood with regal brow,—
 No more, as on the primal sod,
 A creature yet ungrown, but now
 Lord of two worlds, and friend of God!

"This is the species with which we have to deal. It is sometimes said that evolution, as shown in lower spheres, stops with the appearance of man. But the most astonishing product of evolution—its last and strangest chapter—is man himself! man plus an infinite capacity of spirit; man plus machinery, which is but the expression of that capacity; man, whose eyes survey planet and animalcule alike; whose ear catches whispers from all the world; who hears what the past has said; who speaks to the future; whose feet speed over continents and oceans; whose hands tear open mountains, turn rivers from their channels; fill the air with the din of mighty industries; shake the ground with the thunder of battle. Do you say it is the printing press, the steam engine, the dynamo, the explosive mixture, that do these things? I tell you it is man; and these are parts of him!"

But man has always been learning, and always applying knowledge. Why is it that this element of progress has become so much more potent in this present age than ever before? The crude off-hand answer is the true one—there has been a marvelous increase of knowledge, and a corresponding increase in the application of it.

Now this is a cumulative effect, like the annual rise of the Nile. In the high mountains of Abyssinia, ten springs make one brook, ten brooks come together to form one creek, ten creeks form a river, tributary to the Atbara or White Nile, and the Atbara flows to its confluence with the Blue Nile, carrying the muddy contents of all its tributaries. In the dry season, the Atbara itself is but a slender stream, or even a series of water pools only, connected by underground seepage in its sandy bed. But when the heavy rains descend upon its innumerable sources, there are simultaneous floods in all the brooks uniting to larger floods in all the creeks, and so on, until the Atbara is traversed by a mighty wave, advancing like a wall at terrible speed—and the overflow of the Nile has begun, to be felt as a mysterious blessing for 1500 miles. Such is the effect of ten thousand separate springs of human knowledge, when they flow together, to exert their power at once.

Yet this figure is not complete, as a description of the New Age. For the number of the separate sources has been multiplied, through education, in an enormous increase of individual investigators and individual discoveries. I know that in these days it is unpopular to insist upon the rights of the individual. Liberty, property, competition and personal ambition, are all to be sacrificed to collectivism and solidarity. What the result of this wave of socialism may be, no man can yet predict, except so far as history records the rise and fall of similar tides of passion and fashion. But one thing abides sure: the men who discover and apply new knowledge are going to be, as they have always been, the real leaders of the race. No democracy can dethrone them; no juggling with phrases of legislation or declamation can disarm them. They pursue their quiet, irresistible way, while the crowd of partisans, quarreling fiercely among themselves, unconsciously follow these unrecognized yet invincible guides. And there are more of them, a hundredfold, than there ever were before!

And these men are drawn more closely together than ever before. The natural sciences are swiftly becoming one science; and those who utilize by means of science the powers of nature

are beginning to be thrilled with a new sense of brotherhood. They are all *Engineers*, for the mighty enginery of Civilization is in their hands.

The old distinction between abstract and applied science is well-nigh obliterated. The practitioner sometimes follows, sometimes leads, the theorist; it would be more correct, perhaps, to say that they go forward side by side.

Many years ago, Charles Sumner, in the Senate of the United States, proposed an appropriation by Congress, in aid of experiments to test the possibility of telegraphing without a connecting wire. The appropriation was not made; and I remember with what a smile of conscious superiority many regarded that fresh instance of the audacity with which amateurs rush in, where experts know there is no footing. Later, when we studied the lectures of Prof. Hertz and other leaders in abstruse electrical science, how little did we realize that such refinements of theoretical inquiry, swiftly reinforced by practical ingenuity of application, would presently fill with human speech the atmosphere of the world.

Again, the free exchange of knowledge has made its energy well-nigh omnipotent. For in thought, as in mechanics, the measure of energy is not *mv*, but *mv*²—not knowledge alone, but its product when multiplied by the square of the rapidity with which it is communicated.

The old practice of secrecy in applied science has largely passed away. We have found out that when we light another's candle from our own, we have more light ourselves than we had before.

Even business interests, I think, do not, in the long run, favor secrecy. Sir Henry Bessemer's family derived, for several generations, considerable wealth from the manufacture of a bronze powder, the secret of which was jealously kept. But the publicity given to the Bessemer process brought him a much greater reward, and to mankind a greater benefit. You tell me that this was an artificial reward, conferred by the patent law. But the law of patents is but a wise device to secure, through publicity, the double benefit of the immediate use and rapid improvement of an invention, while recognizing the rights and rewarding the labors of the inventor. It is a just bargain as regards the interest of the public; and it is really generous to the inventor. As Sir William Siemens well said, an important invention, given at once freely to the world, might lie in the street for years unnoticed. Some one must be induced by the prospect of a special reward, to take it up, perfect it in practice and push it into the competition of industry.

But I am not discussing the patent law; and I mention it mainly for the purpose of saying that I do not sympathize with the opinion which I have heard in some quarters, that the patentee of a new invention ought not to be permitted to contribute a description of it as a technical paper to a technical society. Under proper restrictions, excluding "puffs," unsupported assertions, and prophecies without experimental proofs and practice, such contributions are among the most valuable that any society can admit into its Transactions.

On the other hand, the maintenance of technical secrets, instead of their free communication, does not, in my judgment, based on half a century of observation, justify itself in the long run. The proprietor of such a secret unconsciously regards himself as beyond the need of improvement, and wakes too late, to discover that he has been surpassed in his art, and that his hoarded advantage has decayed on his hands. Three separate managers in a certain industry once communicated to me, under the seal of confidence, each his own secret process for perfecting a certain product. They were all doing the same thing; and if they had compared notes, they would have found out much sooner than they did, that there was a better thing which they could have adopted.

Apart from all these considerations of immediate business

policy, the advantages of communication and coöperation, whenever practicable, are conspicuous and unquestionable; and their tremendous universal effect is manifested to us in this new age through the activity of technical schools, technical journals, and above all, technical societies.

Perhaps the greatest metallurgical novelty of the 20th century has been the development of electric smelting through the utilization of water-power. Through this industry, Sweden and Norway, rich in minerals but poor in fuel, are coming rapidly to the front, as competitors with those nations which have hitherto been recognized as natural leaders by reason of their supplies in coal. This change would be momentous, if it concerned those two nations only; but lately I found my

professional brethren in Japan, standing tiptoe, as it were, beside the mountain torrents of their Island Empire, watching eagerly, and already beginning to imitate, the metallurgical practice of the Antipodes.

In short, gentlemen, I have arrived, by way of this desultory and imperfect discussion, at the conclusion which I might have stated with eloquent confidence at the beginning—namely, that your Society and similar organizations for the interchange of knowledge constitute the most potent agency and the brightest glory of this New Age.

Whatever you may think of the demonstration, I humbly submit that you ought to be pleased with the proposition!

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE PRODUCTION OF CALCIUM CARBIDE AND CYANAMIDE IN NORWAY

The *Chemiker-Zeitung* (37, No. 6, 65) reports that the plants of the Alby United Carbide Factories, Ltd., of London, in Odda, Norway, will, after the completion of the extension to its works in June, have an annual production of 80,000 tons of calcium carbide, of which, according to a thirty-year contract, 57,000 tons are to be delivered each year to The Nitrogen Fertilizer Co., the rest remaining for the production of acetylene. The Nitrogen Fertilizer Co. has taken over all the shares of the Alby factories, and, in return, has given sufficient of its own stock to be absolutely dominated by the Alby works. The Nitrogen Fertilizer Co. has also acquired the plant of the Northwestern Cyanamide Co., near Odda. The annual capacity now amounts to 18,000 tons of calcium cyanamide. The production is sold out for months to come, for the demand is not only for cyanamide for fertilizer purposes, but also for use in the production of ammonia according to Ostwald's process. There is a reason, therefore, why the Nitrogen Fertilizer Co. has interested itself financially in the Nitrate Products, Ltd., which concern owns the patents on Ostwald's catalytic process for the principal countries.

POTASSIUM SALTS FROM SEAWEED

The *American Fertilizer*, 38, 49, states that the British Consul-General at San Francisco reports that two attempts are now being made to extract potassium salts from seaweed on a commercial scale, but that the industry has so far not passed the experimental stage. One company treats 40 tons of kelp daily, obtaining about 20–30 per cent. of potash from it. The kelp is gathered from the beach, and so contains a good deal of sand. It is dried on the beach by being turned over by hand, and is then burned in an open hearth. The residue is a chloride of potash, which has to be further treated, as only sulfate of potash is used in California. This process requires no fuel, and, though it is crude, yet the results afford good reason for thinking it may be made profitable in time. The other method consists of gathering the kelp in the water by a special cutting device carried on a barge, which ensures that no sand is present, the potash produced being therefore much cleaner. The kelp is treated in closed retorts heated by petroleum. One ton of dried seaweed is estimated to produce about 550 pounds of chloride of potash, 200 pounds of sulfate of potash, 5 pounds of iodine, 200 pounds of fertilizer and 45 pounds of gum, creosote and waste. It is intended to equip the factory at which the kelp is treated with an apparatus for the production of cyanide and chlorate of potash.

THE COBALT OXIDE MARKET

The *Engineering and Mining Journal*, 95, 214, states that the

trade in cobalt oxide is closely controlled, and the price during 1912 was held at \$0.80 per pound without change; for 1913, an advance has been made, and \$0.90 has been announced as the figure for this year's contracts. Except for the imports by the International Nickel Co.'s subsidiaries, there is but little cobalt oxide imported. There is a duty of 25 per cent. on the commercial article, but a few customers adhere to the established European brands and are willing to pay the premium their use entails.

There is some recovery from the Cobalt-district ores, but by no means so great as would be possible with a more widely extended use of the metal. There is no production of the metal as a by-product of copper refining. It is reported that there are over 3,000,000 pounds of cobalt-nickel residues at the Canadian and American refineries treating Cobalt-district ores, but statistics of production are not available.

The Canadian Government is conducting experiments to test the application of cobalt as an alloying material for steel. The results are reported to be encouraging, but it is likely that the final outcome will be only a market on the basis of the prices of nickel, that is, from \$0.30 to \$0.40 per pound for the metal; this conclusion is based upon the chemical similarity, practically speaking, of cobalt and nickel. An outlet for some cobalt products may be looked for in the direction of paint driers and special cutlery, etc., metals; but the principal use now for cobalt is as a coloring for blue glass and for pottery enamel.

THE MARKETS FOR CAUSTIC SODA AND SODA ASH

The following information is taken from *The Chemical Trade Journal*, 52, 3:

A certain amount of caustic soda is imported into France, but large quantities are produced in that country and the exports are almost 15 times as great as the imports. The exports of soda ash are said to be about 20 times as great as the imports. The French caustic soda and soda ash come principally from the northeast in the Department of Meurthe-et-Moselle, a region rich in salt mines. The principal soap-making centers of France are Marseilles (kitchen soaps) and Paris (toilet soaps).

In Germany, soda ash and alkali seem to be controlled very completely by syndicate arrangements, outside of which they can not be had at present. A large number of German concerns produce these articles, the most important being, perhaps, the Deutsche Gold- und Silber-Scheideanstalt, of Frankfort, which controls the Electro-Chemische Fabrik Natrium and the Chemische Fabrik Residua, both of Frankfort. All German houses have given over their export business to Brunner, Mond and Co. and the United Alkali Co., of Liverpool, and these firms seem to be the instruments through which the export trade is distributed.

The imports of caustic soda into Italy average about \$800,000

per year, with a probability of increase as Italian glass, soap, paper and cotton manufacture are further developed. Italy itself produces only a limited quantity of this material, and it is therefore dependent largely upon foreign markets for its supply. Imports of soda ash amount to over \$1,000,000 annually. The imports of crude caustic soda come principally from Great Britain and France, and the same countries lead in exports of soda ash to Italy.

The caustic soda and soda ash used in the Durban district (Natal) is at present purchased from Great Britain and Germany. The consumption of caustic soda in Natal is from 100-150 tons per month, and of soda ash from 40-50 tons per month. There are two soap factories in Durban, and these are the only concerns which use caustic soda or soda ash to any extent.

The imports of caustic soda and soda ash into Japan are practically all from Great Britain. About 10,000,000 pounds of caustic soda and 22,000,000 pounds of soda ash are imported annually for consumption in soap, glass and paper factories.

THE PRESERVATION OF TIMBER

Several papers of interest to the chemical engineer were presented at the annual meeting of the American Wood Preservers' Association in Chicago, January 21-23, 1913.

H. von Schrenk discussed the requirements for successful timber treatment. He pointed out that the amount of material actually treated each year is ten times that of seven or eight years ago. In order to obtain good results from treated timber, he said that the following points must be observed:

- (1) Only perfectly sound timber should be treated.
- (2) Properly seasoned material should be used.
- (3) A good preservative is essential.
- (4) Proper injection as to quantity and penetration is necessary.
- (5) Proper subsequent handling of the timber is essential.

Investigations of premature failures of so-called treated timber have shown that they were attributable, almost without exception, to the non-observance of one or more of these principles. In the early days of wood preservation much timber was treated which was sap rotten. However, the consumer frequently makes demands which cannot be fulfilled, and if they are they are bound to result in ultimate failure. The inspection of material before treatment should be made with great care, and every treating company should be empowered to refuse to treat material which it knows to be defective. The same holds true for improperly seasoned material. In treating green-red oak ties with 2 gallons of creosote oil by the full-cell process, the penetration is insignificant and internal sap rot is bound to occur in a comparatively short period of time.

H. F. Weiss reported the results of an investigation wherein he compared zinc chloride with coal-tar creosote for treating ties. In 1911, there were 9,445,961 ties treated with zinc chloride and 16,510,721 ties with coal-tar creosote in the United States. Zinc chloride and coal-tar creosote, when used under normal conditions, are both effective preservatives of cross-ties, and there is little choice between them so far as annual charges are concerned. Creosoted ties generally cost initially more than Burnettized ties, the cost of treatment being two or three times as great. Creosoted ties last, on the average, longer in the track than Burnettized ties, hence require less frequent renewals and changes in the roadbed. If creosote advances appreciably in price, it will very probably result in stimulating the number of ties treated with zinc chloride.

TAR AS A FUEL FOR OPEN-HEARTH FURNACES

The Indiana Steel Company, of Gary, Ind., has been investigating the use of tar as a fuel for its open-hearth furnaces in the place of producer gas. It is reported that the results of these experiments have been very successful, and at present two fur-

naces in open hearth unit No. 1 are being run exclusively with tar as it comes from the by-product coke oven plant. The tar is handled very much like fuel oil, being atomized with steam in burners similar to those used for oil.

A NOVELTY IN GAS ENGINES

The Gas Age, 31, 77, states that a recent novelty brought out in England was a gas engine fed with powdered coal through a hopper at the ignition end. The coal passes through tubes (2 inches in diameter in a 100 H. P. engine) into the combustion and exhaust chambers, where the heat drives off the gas, which then becomes mixed with the air drawn through the tubes. In the "Low" coal gas engine the inventor claims to be able to produce 1 H. P. with one-half pound of coal and 90 pounds' pressure. If the claims are correct, this "gas producer engine" may interest those who are obliged to dispose of large quantities of coal dust.

THE BRITISH METAL TRADE IN 1912

	IMPORTS LONG TONS	EXPORTS LONG TONS
Copper.....	130,581	57,441
Tin(a).....	60,348	43,663
Lead.....	205,375	58,685
Spelter.....	157,604	10,709
Minor metals (nickel, aluminum, minor metals and alloys).....	7,889	28,549
Mercury.....	1,582	1,079
Pyrites.....	907,157	None

(a) Tin ore and concentrates imported were 28,652 tons, principally from Bolivia and South Africa.

IRON AND STEEL STATISTICS FOR 1912

IRON ORE PRODUCTION AND CONSUMPTION		LONG TONS
Lake Superior.....		48,410,477
Southern States.....		7,590,000
Other States.....		3,485,000
Production in the United States.....		59,485,477
Imports.....		2,200,000
Total supplies.....		61,685,477
Deduct exports.....		1,307,000
Increase in stocks.....		200,000
Consumption.....		60,178,477
The consumption in 1911 amounted to.....		43,571,536

SOURCES OF IRON ORE IMPORTS		Long tons, 11 mo. ending Novem- ber 30, 1912
Cuba.....		1,259,813
Sweden.....		315,796
Newfoundland and Labrador.....		124,585
Canada.....		95,714
Spain.....		83,631
Total imports amounted to.....		1,904,594

PRODUCTION OF PIG IRON		TONS
Foundry and forge.....		6,096,254
Low phosphorus.....		282,359
Bessemer.....		11,385,297
Basic.....		11,394,477
Charcoal.....		347,025
Spiegeleisen.....		96,346
Ferromanganese.....		125,379
Total production.....		29,727,137
Imports.....		125,000
Exports.....		268,000
Consumption.....		30,100,000
Consumption per capita.....		703 pounds

THE STEEL INDUSTRY

The total production of steel for 1912 was about 29,745,000 long tons, of which about 62.5 per cent. was basic and 37.5 per cent. acid. The United States Steel Corporation supplied about 45 per cent. of the steel production of the United States; it earned approximately \$108,178,307, an increase of \$3,822,744 over 1911, although the tonnage of shipments increased about 35 per cent. and the prices rose about \$6.00 per ton.

The iron and steel trades are now in a strong position, and this prosperity seems likely to continue for some time. There was an increase of 20.4 per cent. in exports of iron and steel, including machinery, over 1911, while there was a decrease of 0.04 per cent. in the imports; and the foreign trade for 1913 should be strong.

THE PRODUCTION OF AMMONIUM SULFATE IN 1912

The world's output of ammonium sulfate during 1912 was nearly 1,290,000 tons, more than half as much as the total output of nitrate of soda. This production was thus distributed:

	Tons(a)
Germany.....	465,000
United Kingdom.....	379,000
United States.....	155,000
France.....	68,500
Belgium.....	49,500
Austria-Hungary and remainder of Europe.....	170,000
Total output.....	1,287,000

(a) The figures given throughout refer to ammonia production calculated into its sulfate equivalent, as customary.

It will thus be seen that Germany is now the largest producer, which is partly ascribable to the development of the by-product coke-oven and producer plants, and partly to the increase in German consumption; in 1912, there was a decrease, instead of an increase, in the German exports.

The production in the United Kingdom was as follows:

	Tons
Gas works.....	166,000
Coke, carbonizing and producer gas plants.....	132,000
Shale oil industry.....	61,000
Iron works.....	20,000
Total British output.....	379,000

In 1912, the United Kingdom exported 286,864 tons of ammonium sulfate, 39,333 tons of which went to the United States, 86,659 tons to Japan, and 66,731 tons to Spain and the Canaries. Unless Germany enters into the export trade more prominently during 1913, the producers of the United Kingdom look for an increased demand from the United States and Spain. Prominent British traders still regard the United States position as the crux of the market.

About 215,000 tons of ammonium sulfate were consumed in the United States in 1912, of which amount 60,000 tons were imported. Of the home production, 155,000 tons, about 75 per cent. was produced by the by-product coke plants, and the balance by the bone-black and coal gas industries. The increase in production over 1911 was 28,000 tons, due to the larger operations of the by-product coke industry. At the beginning of 1912, there were 4,624 by-product coke ovens in operation and 698 in course of construction. Additional by-product plants are announced for 1913, and it is expected that the domestic recovery of ammonia will be carried out on a larger scale hereafter. At all events, American manufacturers are not being intimidated, apparently, by either synthetic ammonia or fixed-nitrogen.

THE PETROLEUM INDUSTRY IN THE UNITED STATES IN 1912

Day (*Am. Gaslight J.*, 98, 46; *The Gas Age*, 31, 85) estimates

the crude petroleum production for 1912 in comparison with that of 1911, as follows:

STATE	BARRELS OF 42 GALLONS	
	1911	1912
California.....	81,134,391	87,000,000
Oklahoma.....	56,069,637	52,000,000
Illinois.....	31,317,038	28,000,000
Louisiana.....	10,720,420	10,000,000
West Virginia.....	9,795,464	11,800,000
Texas.....	9,526,474	10,500,000
Ohio.....	8,817,112	8,500,000
Pennsylvania.....	8,248,158	8,000,000
Indiana.....	1,695,289	1,200,000
Kansas.....	1,278,819	1,300,000
New York.....	952,515	700,000
Kentucky.....	472,458	500,000
Colorado.....	226,926	200,000
Other States.....	194,690	500,000
Total production.....	220,449,391	220,200,000

The Engineering and Mining Journal, 95, 152, gives a lower estimate, namely, 218,970,815 barrels.

The decline in production during 1912 exerted an influence on the price; for example, Mercer, Pa., black, quoted at \$0.87 per barrel at the beginning of 1912, was quoted at \$1.53 at the end of the year; North Lima, Ohio, jumped from \$0.84 to \$1.22, Indiana from \$0.79 to \$1.17, Kansas and Oklahoma from \$0.50 to \$0.80, and Electra and Henrietta, Texas, from \$0.53 to \$0.85. Judging from the dividend disbursements by the constituents of the "old" Standard Oil Company, 1912 was a year of prosperity for the Eastern oil companies. While the California oil companies made a creditable showing in dividends, the year closed badly for them, owing to the Standard's refusal to take low-grade oil after the existing contracts expired.

The exports of mineral oils from the United States for the year ended December 31, were 1,736,230,014 gallons in 1911 and 1,844,530,045 gallons in 1912. The exports in 1912 included 173,522,223 gallons of crude; 1,023,681,414 gallons of illuminating oils; 213,559,784 gallons of lubricating oils and paraffin; 175,089,771 gallons of naphthas and gasoline; and 259,276,853 gallons of residuum.

During the year the demand for gasoline greatly increased; there was a considerable extension in the use of oil-driven tractors and agricultural machinery, and the employment of oil engines to reduce power costs in remote districts became more fully appreciated.

Modern refining methods were described in brief during the year by Thomas T. Gray (*The Mineral Industry*, 20, 577), who also indicated some technical problems requiring solution.

CONDITIONS OF THE PLATE GLASS INDUSTRY IN THE UNITED STATES¹

The annual production of plate glass in the United States is about 60,000,000 square feet, about 47 per cent. of which is produced by the Pittsburgh Plate Glass Company and the remainder by the following eleven separate companies:

Allegheny Plate Glass Co., Glassmere, Pa.
American Plate Glass Co., Kane, Pa.
Columbia Plate Glass Co., Blairsville, Pa.
Federal Plate Glass Co., Ottawa, Ill.
Ford, Edward, Plate Glass Co., Rossford, Ohio
Heidenkamp Mirror Co., Springdale, Pa.
Kittanning Plate Glass Co., Kittanning, Pa.
Penn-American Plate Glass Co., Alexandria, Ind.
Saginaw Plate Glass Co., Saginaw, Mich.
St. Louis Plate Glass Co., Valley Park, Mo.
Standard Plate Glass Co., Butler, Pa.

¹ Much of this information has been taken from *The Glassworker*, 31, Nos. 16 and 17 (1913). For a review of the present status of the window glass industry in the United States, see *THIS JOURNAL*, 5, 80.

None of the American product is exported, with the exception of a negligibly small quantity to contiguous territory to supply pressing requirements. The capital invested in the plate glass industry in this country is about \$49,000,000, the smallest concern in the industry having a capital investment of about \$1,000,000. The average number of men employed directly in the industry is about 11,000, but those indirectly employed will equal more than twice this number.

The average cost of manufacturing plate glass in the United States in 1912 was 23.98 cents per square foot without considering depreciation; with depreciation added, but without allowing anything for interest on bonds or capital invested, the cost of plate glass per square foot was 28.45 cents. In 1909, the same cost figures were 28.16 cents and 33.71 cents, respectively. A comparison of the foregoing costs, before deducting depreciation or any interest on bonds or capital, with the average selling prices for the same periods, shows that all glass under five feet was sold at a large loss, while the margin of profit on glass over five feet was but 1.81 cents per square foot in 1909 and 4.66 cents in 1912. If we include depreciation, there existed on sales of plate glass over five square feet an actual loss in 1909 and but 0.19 cent profit per square foot in 1912.

The production of plate glass throughout the world is estimated at 125,000,000 square feet, a little less than one-half of which is produced and consumed in this country. The producing countries in Europe are Belgium, Germany, Austria, France, England, Italy, Spain, and Russia; but Belgium produces more glass than any of the other countries, at the lowest cost, and exports 95 per cent. of its product. The production of all but two of the European plate glass factories is curtailed and prices are fixed under a trust combination; each factory is said to have a capacity of 45 to 50 per cent. more than their present production. Since the organization of the International Convention abroad, the plate glass manufacturers of Europe have prospered and many improvements in machinery have been made, particularly in polishing machines. At present the cost of manufacturing plate glass in Belgium is \$1.06 to \$1.25 per square meter (10.76 square feet), and rough glass is being manufactured at a cost of less than \$0.485 per square meter.

The American plate glass manufacturers are not associated with the European syndicate and consequently the latter has established a low range of prices for the American market. It can undersell competitors in any market in the world and then recoup its losses by adding them to the price of plate glass in markets that it controls, and is in an immediate position to make a strong invasion of the American market.

THE PRESENT STATUS OF THE SUGAR INDUSTRY¹

The year 1912 was indeed a peculiar one in the sugar industry in the United States. In the beet sugar States, with one or two exceptions, the yield was the highest on record, while in Louisiana the output of cane sugar was the lowest recorded for a generation. The "campaign" is now over in the latter State and the product is put at less than 170,000 tons, as against 316,000 tons in 1911. Hundreds of acres of land in the cane parishes were inundated when the levees broke last spring and the young cane was destroyed. Then, too, a freeze occurred early in November, 1912, and another the latter part of the same month. Nevertheless, the Louisiana cane planters have laid plans for a successful campaign in 1913, although during much of the month of December persistent rains retarded field work and delayed the planting of the seed cane.

The 1912 statistics of the beet sugar industry are given in the accompanying table. The heavy beet yield all over the country has had the natural result of enlivening interest in the industry, and there is hardly a State in the beet belt from Ohio

west to the Pacific but has one or more projects on foot with the view to locating new beet sugar factories. Some of the projects are sufficiently developed to insure operation in 1913 if it were not for the tariff situation; in the case of others not so well developed, work has been suspended until the question is definitely settled. It is of interest to note that Texas is rapidly coming to the front as a sugar State.

THE BEET SUGAR INDUSTRY IN THE UNITED STATES FOR 1912

STATE	Factories in operation	Acres harvested	Yield of beets in short tons	Sugar production in short tons
California	10	100,612	980,894	158,432
Colorado	17	142,369	1,683,158	223,181
Idaho	4	18,500	184,000	28,132
Michigan	16	114,012	1,026,208	119,641
Nebraska	2	19,248	213,000	28,150
Ohio	5	27,500	268,214	28,433
Utah	6	36,160	469,000	59,890
Wisconsin	1	23,400	250,000	30,000
One factory states:				
Ariz., Ill., Ia., Kan., Minn., Mont., Nev., Ind.	8	49,800	466,710	63,637
Total	72	531,601	5,541,184	730,166

For comparison, the following European statistics on beet sugar crops for 1912 are available:

	TONS
Russia	1,182,700
Germany	2,604,000
France	893,620

THE PRODUCTION AND CONSUMPTION OF RUBBER IN 1912

The statistics which follow are taken from *The India Rubber World*, 47, 194.

PRODUCTION	
	TONS
South America (East Coast)	40,700
South America (West Coast)	2,000
Central America and Mexico	5,000
Africa	15,000
Assam, Rangoon and Borneo	2,500
Guayule and Jelutong rubber	10,000
Plantation	28,500
All other sources	1,000
Total production	104,700
CONSUMPTION	
	TONS
America	48,000
Great Britain	17,250
Germany	16,000
France	10,000
Russia	7,000
Belgium	2,000
All other countries	8,000
Total consumption	108,250
Excess over production	3,550

IMPORTS INTO THE UNITED STATES

During the fiscal year ending June 30, 1912, 110,210,173 pounds of crude rubber were imported.

For the ten months ending October 31, 1912, 97,308,544 pounds of crude rubber were imported.

From January 1 to November 18, 1912, the United States received 3,572,959 pounds of Ceylon grown rubber.

THE UTILIZATION OF BLAST-FURNACE AND COKE-OVEN GASES.

Gouvy (*Eng.*, 94, No. 2446, 684) states that the French iron and steel works have failed to derive from their waste gases all the advantages possible, largely from having considered the matter from too general an aspect, in capable of studying each

¹ Most of the above information has been taken from *American Sugar Industry*, 16, 21

proposition individually. The course to be adopted should vary with the local conditions, such as the price of fuel, the quantity of coke passed through the blast-furnace, and with the amount of power which can be used in the works themselves and by their subsidiaries, as mines, cement works, etc., all of which afford a field for the use of gases now wasted, in addition to what can be sold to other undertakings. When coke-oven gas is available, as well as that from blast-furnaces, the possible methods of utilization are largely increased. The adoption of regenerative heating has greatly reduced the quantity of gas which it is necessary to consume in the ovens themselves, so that fully 50 per cent. of the total gases liberated are disposable for other purposes.

In the case of the existing French works, Gouvy considers that the program to be adopted must be largely governed by the character of the present steam plant, which it is not always financially possible to modernize. When, on the other hand, new works are being laid out, it is generally feasible to arrange the power plant so that it is operated by the waste gases entirely. It should, in such a case, be possible to operate by the waste gases the blowing-engines, the electric power station of the works, and the rolling mills. If coke-oven gas is also available, it should, moreover, be possible to work thus the reheating furnaces, the steel-furnaces, and the other accessory heating plant.

The first essential to good results with blast-furnace gas is to clean it, so that, as used, it does not contain more than 0.5 gram of dust per cubic meter. This greatly increases the evaporative power of any boiler heated with the gas. Thus, with the uncleaned gas, about 2 cubic meters are required per kilogram of water evaporated, as compared with only 1 to 1.2 cubic meters per kilogram with the uncleaned gas. The great effect of cleaning on the evaporative efficiency is due to the fact that the dust is an excellent non-conductor, and, if present, is deposited upon the heating surfaces, greatly impeding the transmission of heat across them to the water. In a Westphalian works, where the cleaning plant reduces the dust content to less than 0.25 gram per cubic meter, the consumption of gas is only 0.8 cubic meter per kilogram of steam superheated to 250° C.

The same considerations are applicable to blast-heating stoves, on which the dust deposit has a very prejudicial effect. Its presence impedes the transfer of heat from the bricks to the gases, and *vice versa*, and at the same time, if a very hot blast is used, it acts as a flux, making the bricks waste rapidly. Cowper stoves, as usually worked, require from 50 to 60 per cent. of the whole of the furnace gases available, while if these gases are cleaned, the consumption for the same blast temperature will be about only 40 per cent. of the total supply. Since, however, the gas is cooled in the cleaning process, special burners must be provided to insure its ignition. The cost of cleaning to the limit stated should not exceed \$0.00146 per 1,000 cubic feet. For engine-running the gas should be further purified, so as to bring its dust content below, as a maximum, 0.03 gram per cubic meter. To purify the gas sufficiently for use in gas-engines involves an additional outlay over and above the cost of the preliminary cleaning of \$0.00124 per 1,000 cubic feet.

Where coke-oven gas is available, still further economies can be effected. The by-products alone are worth from \$0.20 to \$0.30 per ton of coal coked. If the ovens are fitted with regenerators, about 50 per cent. of the total volume of the gas evolved is available for use elsewhere. This volume varies with the quality of the coal from 250 cubic meters up to 330 cubic meters per ton coked, and its calorific value ranges from 3,500 calories up to 5,500 calories per cubic meter. The coke-ovens at Heinitz, in the basin of the Saar, consume 700 tons of coal daily. With the waste gases a central station of 10,500 horse-power is operated and power is furnished to the surrounding district. The price realized at the switchboard is \$0.01 per kilowatt hour, and the cost of generation, including capital

charges, is below \$0.004. A very suitable use for coke-oven gas is in heating reverberatory furnaces and steel furnaces; blast-furnace gas is hardly suitable for such purposes, although it is being tried in Germany.

ABUSES IN WATER FILTRATION

G. H. Pratt, at the last meeting of the New England Water-works Association, said that the success of a water filtration plant depends, first, upon the selection of the method of purification best suited to local conditions; second, upon the proper operation of the works after installation. Slow sand filtration for a water high in algae is not to be recommended, because of the undue clogging of the beds, but by the use of aeration and prefilters conditions may be greatly improved. Plain sand filtration should not be depended upon to treat a very highly colored water; and the rates of filtration should not be changed quickly, for such a practice tends to disturb the bacterial action at the surface of the bed. A slow sand filtration plant which would handle a given water satisfactorily might, as was the case at Providence, R. I., be installed without covering the beds. In the case of rapid sand filters supervision must be particularly close, and constant chemical control must be maintained.

THE COST OF HYPOCHLORITE DISINFECTION

The following data relating to hypochlorite disinfection is taken from *The Engineering Record*, 67, No. 1, 16:

Commercial bleaching powder packed in sealed drums holding 700 to 800 pounds each, with a guaranteed strength of 36 to 38 per cent. of available chlorine, may be purchased in carload lots for about \$0.0125 per pound. Assuming a disinfectant containing 33⅓ per cent. of available chlorine at a cost of \$0.02 per pound, the treatment of a sewage with 0.1 part per 100,000 available chlorine would require 25 pounds of disinfectant at a cost for chemicals of \$0.50 per million gallons. To produce complete sterilization, the cost would be well over \$19.00 per million gallons for sewage and the effluents from contact and trickling filters, and would vary from \$1.50 to over \$19.00 for effluents from sand filters. To produce a bacterial quality which would conform to the drinking water or 100-10-5 standard, the cost would vary from \$3.75 to over \$19.00 per million gallons for raw sewage and effluents from trickling filters, from \$7.50 to over \$19.00 per million gallons for settled sewage, from \$15.00 to \$19.00 per million gallons for strained sewage and contact filter effluents, would be over \$19.00 for septic sewage, and would vary between \$1.75 and \$9.50 per million gallons for the effluents from sand filters which were not originally of that quality. To produce a bacterial quality to correspond to 1000-100-50 standard, or one which would be about equal to that of the better class of streams not seriously polluted, the cost would be from \$1.75 to \$5.60 per million gallons for raw sewage. These cost estimates are for chemical only, and do not include operating and sinking fund charges.

THE PAPER INDUSTRY OF JAPAN

Paper (January 1, 1913, p. 25) states that after cotton-spinning, the manufacture of paper is the most important industry of Japan.

As raw material, the so-called paper mulberry bush (*Kodzu*), *Broussonetia papyrifera* (mitsumata), serves. While the manufacture of domestic paper is very old, the production of "European" paper was first commenced by the Oji paper mill, working with rice-straw, rags and old paper.

After the Saigon uprising in 1877, as a result of the establishment of numerous printing plants, the demand for European paper increased enormously. The manufacture of domestic paper, mostly conducted with hand apparatus, is carried on principally by the rural population as a secondary occupation,

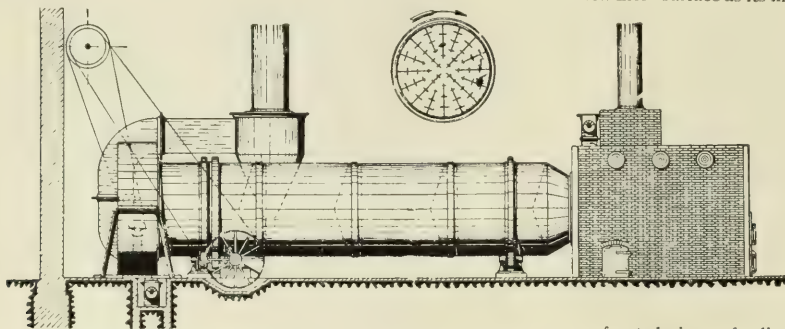
during the dull season. It gives occupation to about 60,000 families. Experimental stations in the most important districts test and select the best raw materials, also imported fibrous material. Guilds supply the country people with raw material and provide for the sale of the product.

Since the acquisition of the island of Saghalien, it supplies the manufacturers with woodpulp, which is cheaper than the domestic vegetable fibers; in Shiraio, too, on the island of Hokushu, a large woodpulp plant has been set up. The manufacture of European paper is conducted chiefly in the large cities, such as Tokio, Osaka and Kobe.

In 1909, there were 27 establishments engaged in the business, with 182 machines and 6,486 employees, turning out 124,000 tons of European paper. The Mitsui Bussan Kaisha, the greatest Japanese business house, has erected at Tomokomai on Hokushu a mill that produces daily 65 tons of newsprint. The product, for the most part, goes to India, Australia and China. Altogether the value of the product of the hand mills is placed at \$8,964,400; of the mills equipped with machines at \$7,497,000. The exports have a value of only \$1,618,400 while the imports amount to \$4,498,200. According to this, Japan consumes, annually, paper to the value of \$19,373,200. In the imports, Germany takes the lead, followed by Austria and England. The paper imported from the two first-named countries consists principally of imitations of Japanese paper.

THE GERLACH DRIER

In the Gerlach drier, System A, the drying is done with hot air. The cut shows the design of a tube-mill drier, provided with partitions arranged as illustrated; these partitions are claimed to effect the finest division and a continuous mixing of the drying material.



In the Gerlach drier, System B, the drying is done with steam. For handling viscous, adherent, sticky or gummy materials, the apparatus consists of a pre-drier and a regular drier.

ARLEDTER'S SAVE-ALL APPARATUS

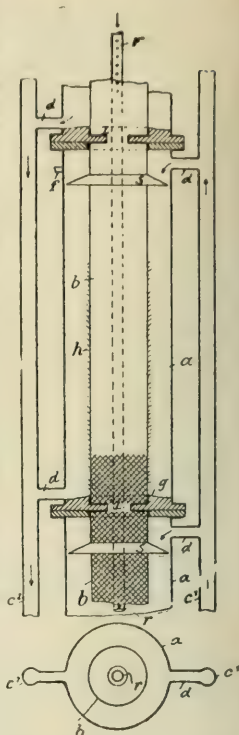
A new apparatus which is said to serve to recover from the waste waters of paper and cellulose mills and similar establishments, the fibrous matter, kaolin, and like materials, suspended in them, has been devised by Fritz Arledter, of Hamburg, Germany. According to the description of this apparatus in *Paper*, January 22, 1913, p. 19, the waste water is discharged in a clarified condition available for immediate reuse, all the fibers, clay, etc., being recovered.

One form of construction of the apparatus is shown in the accompanying illustration: *a* is a pipe of wood or metal of any desired section, in which a sieve-tube (also a felt tube), *b*, is vertically disposed, so that between the tubes *a* and *b* a space is left. For the entrance of the waste water, the side tube *c*¹ serves, and for the discharge of the fibrous substance, the side pipe *c*². Both pipes are connected by supporting spouts, *d*, with the pipe

a. Under the inlet supports, on the sieve tube *b*, deflecting distributors, *s*, are placed. The bottom *g* are inclined towards the discharge spouts. By increasing to any desired extent, the number of double pipes, the filter column can be built as high as desired.

The working method of an apparatus of this character is as follows: If waste water bearing fibrous substances, loading matter, etc., is conducted through the conduit *c*¹ into the filter, the waste water will fall through the spout *d* into the space between the two pipes *a* and *b*, filling it from the bottom upward. The hydrostatic pressure of the rising column of water forces the water through the filter wall *b*, the fibers being deposited on the sieve pipe *b* and themselves forming a filter for the water. The umbrella or roof-shaped ring *s* serves to protect the fiber filter from being washed down from above. The clarified water flows away from inside the sieve pipe, at *b*, for further use.

The fiber filter grows automatically from the bottom upwards. The waste water uses just as much filter surface as its filtration



demands and this, in the development of the tube, is always available. By this means, an automatic regulation of the filter process is created and uninterrupted working is obtained.

If the layer of fibers exceed a certain thickness, retarding the passage of the fluid, the excessively thick portion falls down of itself and its reconstruction commences anew. On the other hand, it is an easy matter to loosen the fiber felt or blow it off, a perforated pipe, *r*, leading into the sieve pipe *b*, through the holes in which steam, water under pressure or compressed air can be forced to such an extent, that the fiber coating on the inside of the pipe can either be loosened or forced completely off. The pipe *r* also serves for washing out purposes. A pipe for the supply of steam can also open into the pipe *f*, whereby the fiber felt *h* forming on the sieve pipe *b* can be loosened and kept permeable for fluids; moreover, the cleansing of the pipe conduits can also be effected, at any time, by the admission of steam.

The displaced fibrous mass drops to the bottom *g* and slips through the discharge spouts into the discharge pipe *c*², whence the mass can be conducted to the hollander or stirring vat. Downwards too, towards the bottom *g*, a layer of fibers is formed which prevents the waste water to be filtered from flowing right off through the pipe *c*². The concentrations can be regulated by throttling of valves. The waste could also be subjected to repeated filtration.

A reverse flow of the waste water to that above described can also be provided for, as regards the regulation of height as well as the flow from one pipe into the other. The separate pipe systems can also be disposed over one another, or in battery

form, alongside of one another, and suitably connected so that a repeated filtration of water and fibrous liquor would be possible. To the side pipe conductors c^1 and c^2 , pumps can be connected; moreover, for the purpose of cleansing the entire plant and detaching the fiber felt, water can be admitted at various points.

At certain points alum solutions can be admitted; also electricity for the purpose of loading the fibers, decomposition of chemicals, etc. The apparatus works uninterruptedly and automatically.

USES OF CAST SILICON

According to *Metallurgical and Chemical Engineering*, 11, 103, silicon is used in the form of pipes for the conveyance of acid gases at a high temperature from stills to condensers, also in the construction of the condensing batteries themselves, proving

more efficient than stoneware owing to its high thermal conductivity and ability to withstand sudden changes of temperature. Silicon pipes are also used for the transportation of hot liquid sulfuric and nitric acids, but it can not be used for hydrochloric acid unless the discoloration resulting from the slight solubility of acid is immaterial. It is used as a lining in centrifugal pumps, acid valves and pipes for the elevation of corrosive liquids by compressed air, and for the construction of plows in ore roasters it is said to have proven efficient. Cast silicon is also being employed in the form of shallow pans and pots for the concentration of zinc chloride solutions, supplanting the enameled stoneware vessels which are rapidly destroyed. Cast silicon ware is said to be produced in practically all shapes required by the chemical industries, such as, for example, pipes, evaporating vessels, receivers, tile, alembics, crucibles, and pump parts.

NOTES AND CORRESPONDENCE

NOTE ON THE INFLUENCE OF THE LIME-MAGNESIA RATIO UPON PLANT GROWTH

Editor of the Journal of Industrial and Engineering, Chemistry:

Starting from the poisonous action of potassium oxalate upon the cellular nucleus and chlorophyll bodies, further considering that the injurious action of magnesium salts on plant cells can be prevented only by calcium salts¹ and finally regarding the fact that a certain excess of calcium salts over magnesium salts retards plant growth, I had inferred that a certain ratio of these two bases must be most favorable for plants.² Many experiments by various authors (chiefly observing cereal and leguminous crops) have confirmed this natural conclusion. Where contradictory results were obtained it could be easily shown that too great a number of plants in the pots had prevented their normal development, since the roots spreading along the walls of the pots were hindered in their normal functions. Indeed such barley plants had reached only a weight of from 2 to 6 grams. A review of the work done in this direction will soon be published in English, to which interested readers may refer.

In the article by Gile and Ageton (*THIS JOURNAL*, 5, 33) it has been pointed out that since citrus, pineapple and sugarcane thrive well on soils with varying amounts of lime and poor in magnesia, the ratio of the two bases seems to have no influence. These are but other examples of apparent exceptions in regard to the lime factor. Such exceptions are the lime-loving plants, e. g., the grapevine, as the writer has pointed out repeatedly.³ These plants are capable of precipitating as oxalate the excess of lime carried into the plant by the transpiration process. Thus an unfavorable ratio of lime to magnesia in the cells is avoided since the lime in the form of insoluble oxalate cannot further participate in the physiological processes. Now it is well known that the pineapple plant and citrus show a large amount of calcium oxalate crystals in the cells. It is not yet known whether cane grown on soils rich in lime and poor in magnesia stores crystals of calcium oxalate. Among the graminæ plants this is only occasionally observed, as with millet.

It has been stated in the article referred to that cane grows well on soils containing only traces of magnesia. In this case inquiry should have been made as to the manure applied, since tankage, cottonseed meal and stable manure contain so much magnesia and lime in an easily available form that the plants thus manured need not depend on these bases in the soil, in fact,

become almost independent of the lime factor in the soils, as I have pointed out long ago.¹ When, however, fields are manured exclusively, as is often done, with inorganic manure, and only with regard to nitrogen, potash and phosphoric acid, then the ratio of lime to magnesia² present in the soil will certainly exert an influence on development.

The yields of cane on different soils with different ratios of lime to magnesia were compared in the article referred to and the conclusion drawn that there exists no relation between this ratio and the cane production. This conclusion was not justified since no information was procured as to the manuring and the amount of tankage applied, and the quantity of lime and magnesia thus supplied to the plants in an easily available condition was not taken into account. Also, yields on different soils with different ratios of lime and magnesia and different manure cannot be compared; only those on different plots of one and the same soil in which different ratios have been produced are comparable. Further, the opinion that only compounds contained in soil solutions are available to plants—which is certainly erroneous—led to the erroneous conclusion that all plants in the field were independent of the ratio of lime to magnesia. Voelcker in England, Bernardini in Italy, Warthiadi in Munich, as well as the writer and his co-workers, have all experimented with various soils and observed the great influence of their various ratios of lime to magnesia upon the development of cereals and other plants.³

It was further asserted that it is chiefly the ratio of lime to other mineral nutrients that comes into play and not that to magnesia. The literature on the subject disagrees with this assertion.⁴ But in order that the lime factor can fully make its impression upon the development of plants, the amount of easily available phosphoric acid is also very important, as I have repeatedly mentioned.⁵

SUMMARY

I. Citrus and pineapple are lime-loving plants; an excess of lime absorbed by these plants can be rendered innocuous by the transformation of that excess into oxalate. Thus a properly working ratio of lime to magnesia is secured in the cells when the plants grow on soils too rich in lime. Hence the view, that

¹ *Bull.* 45, 70, *Landw. Jahrb.* 35, 532

² It is supposed that the availability of both these bases is equal or nearly so.

³ These soils were in our case surely not "alkaline" soils. Compare also the confirmation by Portheim and Sauer in Vienna and of Hanstein in Christiania.

⁴ *Landw. Jahrb.* 35, 533 (1906); *Bull. College Agr., Tokyo*, 7, 396. *Flora*, 102, 110.

⁵ *Bull.* 1, 16, Bureau of Plant Industry, and *Landw. Jahrb.*, 1902, 569.

¹ Potassium salts can only retard it. Cf. *Flora*, 102, 110.

² *Bull.* 45, Bureau of Plant Industry, Washington, 1903, p. 43, and *Landw. Jahrb.*, 35, 539.

³ *Bull.* 45, 68-70.

the favorable development of these plants on soils very rich in lime and poor in magnesia would be a proof against the influence of a certain ratio of lime to magnesia in soils upon other plants which do not produce oxalates, is not tenable.

11. Experiments upon the influence on cane growth of different ratios of lime to magnesia produced in one and the same soil, *manured exclusively with mineral compounds*, have thus far not yet been made. Hence the opinion that the growth of cane is independent of that ratio is not justified.

OSCAR LOEW

HYGIENIC INSTITUTE
MUNICH, GERMANY

AN IMPROVED METHOD OF CRUDE FIBER ESTIMATION

Editor of the Journal of Industrial and Engineering Chemistry:

This crude-fiber method is an improvement on the Morgan P. Sweeney modification of the official method, the improvement consisting in filtration through asbestos and sand in a Gooch crucible, treatment with hydrochloric acid, washing without transfer, and ignition in the Gooch crucible. The details are as follows:

To a 1- or 2-gram sample add 200 cc. of boiling 1.25 per cent. sulfuric acid, and boil for 30 minutes.

Neutralize with 10 per cent. sodium hydrate, using phenolphthalein as an indicator; add 200 cc. of 2.656 per cent. boiling sodium hydrate; make volume up to 425 cc. and boil for 30 minutes.

Filter through a porcelain Gooch crucible containing an asbestos pad and 10-12 grams ($\frac{1}{2}$ inch) of very fine acid-washed sand, compacted by water and suction. Treat with hydrochloric acid; wash with hot water until free from chlorides, and then with alcohol and ether; dry, weigh, ignite and weigh.

Sand satisfactory for this purpose has been purchased from the Berkshire Glass Sand Co., of Cheshire, Mass. Coarse sand was found not to be useful, the reason being that it allows the fiber to pass through and then to clog the asbestos pad.

The improved method usually gives higher figures than the official method. In general the results check, one with another, more satisfactorily, and the method is very much easier to use.

The unsatisfactory character of the official method is too well known to require comment. This new procedure eliminates all transfer of the sample and also the unstandardized cloth strainer, for which it substitutes a filter which is thoroughly efficient, and which at the same time allows of very rapid filtration of solutions such as those from linseed and cottonseed meals which are very difficult of filtration by any other method. The use of hydrochloric acid facilitates the final washing.

A microscopical examination of the crude fiber and the filtrates from the official and from our modified methods showed that the higher results obtained by the latter were due to undissolved woody and chitinous particles which passed through the linen but which were retained by the sand and asbestos. In the products examined there was no evidence of contamination of the crude fiber as determined by the improved method by gummy or protein substances.

Objection to the Sweeney method has been raised on account of difficulty with the colored extracts of some feeds in determining the neutral point. This objection is not insuperable in any case and in using this method with a wide range and considerable number of products we found that it was in rare instances only that the color of the extract interfered with the use of the indicator.

The slow filtration by the Sweeney method is entirely overcome in our modification.

Objection has also been raised to the Sweeney method on account of possible interference of the fat with the solution of

the acid and alkali-soluble constituents. This possibility, however, has not been proved to affect results appreciably.

Whatever the method under consideration, we are unable to judge of its accuracy by comparison with the official method because of the lack of definiteness as to the character of the cloth strainer and because of the incomplete retention of the crude fiber of some products by such a filter.

Below are a few figures by this method, and the official method. The sample in each case weighed 1 gram. The figures are weights in grams of crude fiber.

	Official method	Modified method		Official method	Modified method
Cowpeas	0.0544	0.0568	Oats, grain	0.1215	0.1217
	0.0560	0.0564		0.1212	0.1218
	0.0570	0.0554		0.0837	0.0856
Linseed oil meal	0.0922	0.1110	Wheat bran	0.0830	0.0868
	0.0908	0.1118		0.0324	0.0342
	0.0910	0.1112		0.0341	0.0342
Corn meal	0.0228	0.0272	Patent flour	0.0010	0.0021
	0.0212	0.0280		0.0012	0.0028
	0.0238	0.0272	Gluten feed	0.0892	0.0886
Soy beans	0.0470	0.0482		0.0891	0.0881
	0.0472	0.0484		0.0705	0.0710
Distiller's grain (corn)	0.1232	0.1239	Cottonseed meal	0.0703	0.0720
	0.1228	0.1240			

E. B. FORBES AND J. E. MENSCHING

OHIO AGRICULTURAL EXPERIMENT STATION
WOOSTER, Dec. 27, 1912

AMERICAN MINE SAFETY ASSOCIATION

As the result of a conference which was held under the auspices of the United States Bureau of Mines last September, by two men who are interested in the saving of the lives of miners, there has been formed a society known as the American Mine Safety Association, with headquarters at 40th and Butler Streets, Pittsburgh, Pa. This association, which is now enrolling among its members the leading coal and metal mine operators, mining engineers, and mine safety engineers of the country, has for its purpose the conservation of the life and health of the miner and a reduction in property loss due to explosions or fires in mines. It will attempt to place before the miners standard methods to be used in rescue work and in first aid to the injured.

The work of the Bureau of Mines in reducing the number of deaths in the mines has led to the adoption of many different types of rescue apparatus, such as the oxygen helmets which the rescuers wear in a gas-filled mine, and also to the use of many different methods of resuscitation and first aid to the injured. Hundreds of mines within the last three or four years have been equipped with rescue apparatus, rescue corps, and first-aid corps. Many of these men who are called upon in emergencies have developed their own ways of doing things and it is the opinion of the organizers of this association that the most efficient methods and apparatus should be found through actual use and recommended to the mining industry as a general standard.

H. M. Wilson, the engineer in charge of the Experiment Station of the Bureau of Mines at Pittsburgh, has been selected as chairman of the executive committee of the Association and has been instructed to carry on the work of organization.

There were 2,719 persons killed in the coal mines of the United States during the year 1911, and there were 9,106 seriously and 22,228 slightly injured. Nearly an equal number of men were injured in metal mines and quarries.

In the hope of reducing the number of these accidents and of shortening the period of disability of the injured, it was felt that there should be greater uniformity in methods of conducting rescue operations in mines after explosions, fires, or other disasters, and of giving first aid to the injured.

The Director of the United States Bureau of Mines therefore called in Pittsburgh, September, 23, 1912, a National Mine Rescue and First Aid Conference. About half a hundred men concerned in safety in mines attended. There were nearly an equal number of mine operators, mine surgeons and mine safety inspectors and rescue men; they represented geographically all of the principal mining regions from Pennsylvania to Colorado, and from Alabama to Michigan. They voted to form a permanent organization and to hold the first annual meeting in the fall of 1913.

THE ANALYSIS OF ORGANIC DYESTUFFS

Editor of the Journal of Industrial and Engineering Chemistry:

Sub-Commission XI of the International Commission of Analyses, appointed to study the question of the analysis of Organic Coloring Matters, has examined the possibility of unifying the analytical methods at present employed, and whether such unification would be of practical use. Reports have been received from various countries, and the Committee reporter has arrived at the conclusion that the unification of the methods employed in the analysis of organic coloring matters is not possible at the present state of the industry, and would not be of any practical use.

However, an international agreement might be advantageous in certain cases, such as that of those organic dyestuffs which are taken as standard in the levying of custom duties. Such an agreement would protect both exporter and importer and prevent disputes. It might also be of use in the dye industry in the case of certain dyestuffs. So that if the unification of the methods of analysis of all organic dyestuffs is not feasible, at least useful work might be done as regards certain special cases.

The International Commission of Analyses, presided over by Professor Lindet, after taking cognizance of the reports on this subject presented at the Eighth International Congress of Applied Chemistry held at New York in September, 1912, adopted the following resolution: "That Sub-Commission No. XI, in pursuance of its work, shall investigate special cases, in which the unification of the methods of analysis of organic dyestuffs offers some interest from the international standpoint."

I therefore beg you, Mr. Editor, to request, through the medium of your esteemed paper, all the heads of official analytical laboratories, and factory laboratories, as well as all those who are interested in this branch of chemistry, to have the kindness to direct the attention of our Sub-Commission (or the President or one of the members) to any case in which they consider that an international agreement would be desirable in the direction that we have indicated above. The members of the Sub-Commission for the United States are: Dr. B. Hesse, New York; Prof. Dr. S. P. Mulliken, Boston; and L. A. Olney, Lowell, Mass.

FRÉDÉRIC RÉVERDIN, *President*

GENEVA, SWITZERLAND

PLATINUM THIEF

Fellow Chemists: In THIS JOURNAL, 5, 82, I published a brief account of the recent theft of platinum from the laboratory of this Company and others, the capture of the man believed to be the thief, and the status of the prosecution.

In the recent county court session at Easton, Pa., Leon Cohn, defendant, was found guilty of stealing platinum from this Company. He received a sentence of two years imprisonment and a fine. The evidence admitted in the trial was restricted to that attaching directly to the circumstances attending his visits to this laboratory, and his arrest at Sparrows Point, Md.

After the jury's verdict, Cohn admitted to the court that he had stolen platinum, and declared that he would steal it again if he had the opportunity. I make this statement as a warning, and suggest, with emphasis, that those who have similar cases

against him should not forget to start their prosecutions in proper time. Now that one conviction has been secured, subsequent cases should be relatively easy.

Before this case came to trial, one dealer in New York City was found who had bought part of Cohn's stolen platinum, and another who had, at least, sent him money. Neither of these parties would appear as a witness at the trial. Incidentally it may be remarked that there is little hope of any platinum stolen by Cohn ever being recovered. Most of us, doubtless, have entertained a false sense of security in the possession of platinum entrusted to our care, in the belief that it would be exceedingly difficult for a thief to dispose of it. Years ago there probably was more reason for this belief. Being in possession of the evidence secured in the course of this investigation, I am convinced that the disposal of platinum at the present time is a comparatively easy matter. The wide-spread and increased use of platinum in the dental and jewelry trades is substance for reflection in this regard.

It would seem unnecessary to remark that in the future there should be no recurrence of such a long series of platinum thefts by a single man, as have been perpetrated by Leon Cohn. A quiet warning, which was so effectively issued in the present case through the Secretary's office of the American Chemical Society, should result unflinchingly in the apprehension of the criminal, or cause a cessation of his activities.

In conclusion, I wish to thank the many chemists who have endeavored to cooperate in the prosecution of the case just completed.

I have a considerable mass of correspondence relating to the matter, and any part of it will gladly be loaned if it may prove of value in the future.

Members of the State constabulary, who assisted in our case, will be glad to cooperate with officers at other points where it is desired to institute prosecutions. Any communications, which may properly be referred to them, will be forwarded as received.

R. J. WYSOR, *Chief Chemist*

BETHLEHEM STEEL COMPANY
SOUTH BETHLEHEM, PA.

MAGNESITE IN LOWER CALIFORNIA

Consul Lucien N. Sullivan, La Paz, Mexico, reports the presence of beds of high-grade magnesite in the region of Magdalena Bay. Analysis shows this product to contain 92 per cent. pure magnesium carbonate. The largest bed has an area of some 30 acres and is located on Margarita Island. Denouncements have been made on 13 deposits, covering a total area of 250 acres. There are 50 acres on Cedros Island.

Compañía de Desarrollo y Explotación de la Baja California, with main offices at San Diego, Cal., will install one calcining plant on Cedros Island and another on Margarita Island, each to have a capacity of 200 tons per day. Experts who have examined the properties, taken measurements by sinking numerous test holes, and estimated the contents of the beds, report that there are more than a million tons in sight. The material is so hard that it must be blasted before it can be removed.

The U. S. Geological Survey states that the only deposits of magnesite in the United States which have been commercially utilized are those situated in the valley and coast counties of California. The total production reported in 1911 was 9,375 tons of crude magnesite, valued at \$75,000, estimating the average value of the ore at \$8 a ton. This is somewhat higher than the price fixed for the crude ore in 1910 (when the 12,443 short tons of crude magnesite produced were valued at \$74,658), but is thought to be the present value of this product as mined and laid down at the point of shipment. Most of the magnesite produced in California is calcined at the mine, thereby reducing

its weight approximately one-half and correspondingly increasing the value of the product as shipped.

The principal markets of the Eastern States and the Mississippi Valley are supplied by importation. Imported magnesite is quoted at \$10 to \$11 per long ton for the raw and \$30 to \$35 for the calcined and powdered product at New York. Imports for the year 1911 amounted to 122,075 short tons of calcined and 12,974 short tons of crude magnesite, not including the refined magnesite salts used for medicinal and other purposes.

Crude magnesite is used for the manufacture of carbon dioxide gas. Magnesium chloride is an excellent bleaching agent. The light carbonate of magnesia (*alba levis*) is used for medicinal and toilet purposes. The sulfate, known as Epsom salts, is mainly used in warp sizing or weighting in cotton mills, and lesser quantities are used for medicinal purposes. The hydrate is used in sugar manufacture.

Calcined magnesia, generally in the form of brick, is now universally recognized as the best material for lining basic open-hearth furnaces, copper-smelting furnaces, cement kilns, etc. It may be employed to advantage wherever high temperatures and chemical reactions are usually detrimental to dolomite-chromite, and silica brick. It is also used in the manufacture of boiler and steam-pipe covering, stoppers, sleeves, hot-metal ladles, tuyères, and nozzles.

Sintered magnesite tubing of assorted sizes is regularly made for chemical and electrometallurgical work; magnesite crucibles are made of various forms and different degrees of fineness. A coating of crushed magnesite is sometimes laid on hearths for heating steel stock for rolling to prevent the scale formed from attacking the fire-brick of the hearth.

As a building material calcined magnesite is most largely used for constructive fire-proof flooring and tiling, but it is also made into artificial stone and marble, hollow tile, drain-pipe, partitions, staircases, wainscoting, tanks, trays, wash-tubs, ornamental moldings, building blocks, cement, doorways, window casings, etc. Experiments are under way in California for making a protective paint for both wood and metal work to prevent corrosion or fire. It has lately come into quite extensive use as a flooring in steel railroad cars, being mixed with other substances to make it plastic so it may be laid in one continuous piece without seams. The fine waste of the crude ore mined is now being utilized in the California chicken ranches as a substitute for oyster-shells and other substances fed to fowls for hardening the egg-shells.

DEFECTIVE ARTIFICIAL SILK

The annual report just issued by the German Imperial Testing Department states that quite a number of samples of defective artificial silk were received during the past year for examination. The faults in the material took the form of chalky-looking places which were without luster and very tender. In all cases the goods had been produced by the guncotton process. The defects were traced to the presence of free sulfuric acid, due to the decomposition during storage of cellulose sulfate compounds formed in the process of manufacture. A number of apparently pure silk goods were also tested in the laboratories for artificial

silk, and in several instances this was found to be present in a large proportion. The mixture is stated to have been very difficult to distinguish from pure silk by mere visual examination even by experts, the adulteration having been made during the throwing operation by doubling fibers of artificial silk along with those of the natural silk, and the pieces woven from the yarn so produced.

INCREASED WORLD'S CONSUMPTION OF NITRATE

The half-yearly report of W. Montgomery & Co. gives the increase in the world's production and consumption from year to year since 1902.

Year	Production Tons	Consumption Tons
1902	1,351,000	1,259,000
1903	1,462,000	1,412,000
1904	1,535,000	1,447,000
1905	1,728,000	1,547,000
1906	1,795,000	1,636,000
1907	1,818,000	1,658,000
1908	1,940,000	1,732,000
1909	2,077,000	1,938,000
1910	2,427,000	2,241,000
1911	2,482,000	2,355,000
1912	2,540,000	2,504,000
Total	21,155,000	19,729,000

Production and consumption have been running a close race at times, especially during the past four years, and it is quite possible that the coming season will feel the effect of a limited supply. At present it seems that there is very little margin for expansion in consumption either in Europe or America.

Imports of nitrate of soda into the United States in the fiscal year 1912 amounted to 481,786 tons, valued at \$15,427,904, as against 546,394 tons in 1911, valued at \$17,101,155.

THE EFFECT OF EXPOSURE ON BITUMENS—A CORRECTION

Editor of the Journal of Industrial and Engineering Chemistry:

My attention has been called to the fact that the article on "The Effect of Exposure on Bitumens" appearing in *THIS JOURNAL* 5, 15, has been credited to the Institute of Industrial Research, while the work described in this paper was done in the laboratory of the U. S. Office of Public Roads. Kindly note this correction in the columns of your Journal.

PRÉVOST HUBBARD

THE DETERMINATION OF "VOLATILE" IN COAL—A CORRECTION.

In my article under the above title, *THIS JOURNAL*, 5, 169, the first ash determination should be 5.40 per cent. instead of 4.40 per cent.

FRED C. WELD

THE DETERMINATION OF LIME IN COW FECES—A CORRECTION

In *THIS JOURNAL*, 5, 37, second column, foot-note 2 should read Fresenius's "Quant. Anal.," Vol. II, p. 808.

R. ADAMS DUTCHER

BOOK REVIEWS

Transactions of the American Ceramic Society. Volume XIV. H. F. STALEY, Editor, Columbus, Ohio.

This well-appearing volume of 888 pages represents the work of the American Ceramic Society for the year 1912 and illustrates the important field being covered by this active organization.

The object of the society is the study of the raw materials and products of the silicate industries, comprising the entire field of clay, glass and cement technology. Practically all of the important work being done in this field in the United States appears in these transactions which are indeed a credit to the modern spirit pervading our American industries. Among the papers

we find reports of work done upon a great variety of subjects.

The titles of the contributions are as follows:

- "Influence of Silica and Alumina on Porcelain Glazes," by R. T. Stull.
- "The Plasticity of Clay," by F. F. Grout and F. Poppe.
- "Results of Tests on some Bricks from the Provinces of Western Canada," by H. Ries.
- "Some Data on the Deformation Points of Feldspar Mixtures," by A. S. Watts.
- "A Study of Glaze Composition on the Basis of 'Norms,'" by R. C. Purdy.
- "Downdraft Kiln Bottoms," by T. W. Garve.
- "Colors Produced by Nickel Oxide in Ceramic Mixtures Containing Zinc Oxide," by F. K. Pence.
- "Drying Defects in some Cretaceous Clays of the Great Plains Region of Canada," by Jos. Keele.
- "The Influence of Composition of the Stain in the Production of Red from Chrome-Tin Pink Stains," by R. C. Purdy.
- "A Comparison of the Rattler Test and the Sand Blast Test for Paving Bricks," by Edward Orton, Jr.
- "A Thermal Study of Boric Acid-Silica Mixtures," by A. V. Bleining and P. Teetor.
- "The Behavior of Granular Limestone in Burned Clay," by C. F. Binns and M. A. Coats.
- "The Production of Black Spots upon Terra Cotta Glazes," by C. W. Parmelee and R. Heidingsfeld.
- "A Glaze Imitation of Granite," by R. Heidingsfeld.
- "The Relation between Manufacture and Properties of Refractory Clay Wares," by W. Stout.
- "Production of Vitrified Black and Chocolate Floor Tile," by R. C. Purdy.
- "High Voltage Insulators and High Potential Testing," by E. T. Montgomery.
- "The Effect of Temperature on the Dielectric Strength of Porcelains," by G. Weimer and C. T. Dun.
- "The Relation between the Crushing Strength and the Porosity of Clay Products," by G. H. Brown.
- "Studies of Flint Clays and their Associates," by S. L. Galpin.
- "Examples showing the Usefulness of the Rational Analysis of Clays as a Means of Controlling Glaze Fit," by R. C. Purdy.
- "Note on the Fuel Consumption of Some Whiteware Kilns," by T. Gray.
- "Note on Load Tests Made on Magnesite, Chrome and Silica Brick," by G. H. Brown.
- "Note on the Specific Heat of Clay," by J. M. Knot.
- "Bodies for Inverted Mantle Rings," by R. L. Clare.
- "Light Green Chromium Stains," by A. R. Heubach.
- "Kaolin Mining in the South Appalachian Mountains," by A. S. Watts.
- "An Apparatus for the Determination of the Expansion Coefficient of Solid Bodies," by P. A. Boeck.
- "Recent Developments in the Refractories Industry," by F. T. Havard.
- "A Comparison of Ten White Enamels for Sheet Steel," by R. D. Landrum.
- "The Cause and Control of Crazing in Enamels on Cast Iron," by H. F. Staley.
- "The Testing of Paper Clays," by C. S. Gwinn.
- "Investigations on the Dielectric Strength of Some Porcelains," by B. S. Radcliffe.
- "The Working of Some Montana Clays," by R. R. Hice.
- "Notes and Data on Operation of the Denny-Renton Double Deck Tunnel Drier," by S. C. Karzen.
- "The Power Consumption of Brick Machinery," by R. R. Hice.
- "Design of an Economic Furnace for Tunnel Drying," by S. C. Karzen.
- "A Note on the Accidental Pink Discoloration of a White Enamel for Terra Cotta," by D. F. Albery.
- "Some Chemical Reactions of Interest to the Plate Glass Chemist," by F. Gelstharp.
- "Behavior of an Acid Glass in a Tank Furnace," by J. M. Knot.
- "Solubility of Some Salts in Glass," by F. Gelstharp.
- "Matte Glazes," by R. C. Purdy.
- "A Theory for the Cause of Mattiness in Glazes," by F. K. Pence.
- "Microscopic Examination of Twelve Matte Glazes," by H. F. Staley.
- "The Dehydration of Clay," by G. H. Brown and E. T. Montgomery.
- "Philippine Pottery," by C. H. Crowe.
- "The Chemical Role of Boron in Glazes," by R. C. Purdy.
- "The Replacement of Tin Oxide by Antimony Oxide in Enamels for Cast Iron," by R. E. Brown.
- "The Necessity of Cobalt Oxide in Ground-Coat Enamels for Sheet Steel," by R. D. Landrum.
- "Cobalt Colors Other than Blue," by R. T. Stull and G. H. Baldwin.
- "Notes on the Performance of a Producer Gas Fired Continuous Kiln," by W. D. Richardson.
- "Note on the Dissociation of Calcium Hydrate," by R. K. Hursh.
- "Oil as a Fuel in Burning Ceramic Wares," by J. K. Moore.
- "Note on the Relation between Preheating Temperature and Volume Shrinkage," by R. K. Hursh.
- "The Nomenclature of Clays," by C. F. Binns.

"Observations on the Effect of Pressure on the Vitrification of Clay," by L. Parker.

"The Effect of Acids and Alkalies upon Clay in the Plastic State," by A. V. Bleining and C. E. Fulton.

"Note on Terra Cotta Glazes," by C. W. Parmelee and R. Heidingsfeld.

"The Melting Points of Pyrometric Cones under Various Conditions," by S. Geijsbeek.

The printing of the text is excellent and the illustrations, including three color plates, are very satisfactory. From the secretary's report it appears that the society is in a flourishing condition which, after all, is the most valuable criterion of the activity of an organization.

A. V. BLEININGER

Preparation and Uses of White Zinc Paints. By P. FLEURY.

Translated by DONALD GRANT. Scott, Greenwood & Son, London. D. Van Nostrand Company, New York. Price, \$2.50.

The author, Mr. Fleury, is a French master painter, with a fondness for scientific study but without technical training. He frankly states that his predilections are for lead paints rather than zinc but, as the French Government has ordered the use of white lead to be discontinued after July 20, 1914, he has experimented to determine the best way of using zinc oxide, and this book gives the results.

The practical part of the book is the best, his formulas for paint and directions for its application being good. He calls particular attention to the necessity of varying the proportions of oil and turpentine to pigment and to each other, to suit the different pigments and classes of surface to be painted. His theories, however, are frequently questionable. He speaks of different grades of zinc oxide as varying in fineness, weight and durability. This is not correct, the variation in the gravity of commercially pure zinc oxide is less than the probable error in the determination. The final size of grain is the same in all cases, but the grain seen is always an aggregation. These aggregations vary considerably in size and compactness, which conveys the impression of differences in size and gravity. In speaking of the oxides commercially free from lead, he states that the lower grades are more durable. This again is a mistake, the grading is simply by color, except in the case of White Seal, and all are equally durable. With leaded zincs the case is different; they are graded both by color and lead content, which varies from 3 per cent. to 40 per cent. lead sulfate. Regarding the relative values of these as protective coatings, we have not much information, but what there is indicates that the presence of lead sulfate is not injurious. Where the paint is used for decoration the lead salts are all undesirable, although the sulfate is less so than the carbonate or hydroxide.

The chapter on the manufacture of zinc oxide is very incomplete as it does not mention the direct process by which most of the zinc oxide used is made.

He very properly calls attention to the inferiority of mixtures of zinc sulfide and barium sulfate to lithopone, and speaks well of the latter for inside work, while condemning it for outside. In this he agrees with the general opinion, although recent improvements in its manufacture seem likely to modify this conclusion.

Covering power is defined as *hiding power*, and the author says "that paint which masks the under surface best with the least thickness of paint, is the one that has the greatest covering power." An excellent method is described for a practical test, and the result of a very careful set of experiments by Lenoble of Lille is given. These show that weight for weight, or bulk for bulk, zinc oxide has a greater covering power than white lead, but, owing to its requiring more oil, it needs a greater number of coats to give an equal amount of pigment on the same surface.

There is a good chapter on grinding in which the author points out the necessity of having all materials perfectly dry, of keeping the oil at a normal and uniform temperature, and of properly regulating the speed of the mills. He states what is perfectly

true, but not always recognized, that good materials may make a bad paint if improperly ground.

An excellent account is given of the experiments of the Dutch Commission and of the legislation prohibiting and regulating the uses of white lead. The author freely admits his prejudice in favor of lead, but endeavors to be, and in the main is, fair in his comments.

The last chapter is on "Qualitative Analysis," and it is unfortunate that it was written, as the author's knowledge of chemistry is rudimentary. The translator has endeavored to make up for this by numerous foot-notes to this chapter, pointing out the errors and omissions in the text, and thereby partly makes up for the curious and involved English which he frequently uses.

With the exception of the chapter on "Analysis" and some of the theories advanced, the book is good, but hardly a safe one to put in the hands of a non-technical reader. For the technologist who wishes to learn more of the painter's view of pigments, it can be recommended.

GEORGE C. STONE

Refractories and Furnaces. By F. T. HAVARD. McGraw-Hill Book Co., New York, 1912. Price, \$4.00.

This timely work deals with a subject of prime importance to metallurgy and aims to present the principles underlying the production and use of refractories. The introduction gives a brief historical review of clay working, of which the part dealing with the development of the American fire-brick industry is the most satisfactory. In Chapter I, the usual classification of acid, basic and neutral refractories is adopted. The table of formation and melting temperatures of silicates in Chapter II might have been greatly enlarged. The description of the manufacture of silica brick, Chapter III, is concise and satisfactory. The figures given for the burning of silica brick give rise to a discrepancy; in one place it is said that the temperature rises as high as 1600° C., in another that it is 1500° or 1700°.

The treatment of the subject of refractory clays is not as satisfactory as might be wished and it is evident that the writer is on unfamiliar ground. Thus considerable attention is given to the old Bischof refractory coefficient which has been discarded long since. The work of Richters, Seger, Cramer, Ludwig, Mellor, Rieke, Flach, on fire clays is not mentioned. The use of waste gases from kilns for steam raising is not common in this country. The Cassel kiln cannot be said to be an economical kiln; if anything it is less so than the downdraft. Chapter V, dealing with the basic and neutral refractories, is interesting and instructive. Chapters VI, VII, VIII and IX, dealing with the construction of metallurgical furnaces and the use of refractories, form a valuable summary of this subject. This applies particularly to copper furnaces. The use of magnesium oxychloride and carborundum as an acid-proof mortar for the Glover tower, etc., does not seem promising nor as satisfactory as the barium sulfate-water glass cement frequently employed.

In Chapter X instances of the use of refractory bricks in industrial furnaces are briefly described. More attention might have been given to glass furnaces where the proper use of refractories is exceedingly important. Some interesting facts have been compiled in Chapter XI, the use of refractory mortars and paints. The use of coatings for rendering furnace walls more heat-resistant as quoted on page 218 is misleading.

In Chapter XII, refractory hollow ware, the treatment of retorts is quite satisfactory; no mention is made of glass pots. Chapter XIII, on the testing of refractories, is inadequate. No mention is made of Purdy's method of classifying fire clays. The statement that "the refractory must stand a temperature of at least 50° C. above that at which it is used" needs elaborate amplification. The viscosity of refractories at furnace temperatures is an important property which requires discussion and which is not satisfactorily measured by the Cramer test. The

Deville furnace is not satisfactory in this day of carbon resistance furnaces. Chapter XIV contains compilations of the work of Wologdine, Hering and others. The subject of heat measurement is considered in Chapter XV. While two diagrams are given of the electric resistance pyrometer, the subject of the thermocouple is dismissed too briefly. Mention might have been made of the Holborn Kurlbaum optical pyrometer. The book concludes with a chapter on common bricks.

The work as a whole is interesting and while not quite satisfactory to the specialist in silicate technology, fills an important need on the part of the user of refractories. The typographical execution of the book is excellent.

A. V. BLEININGER

The Science of Hygiene. By WALTER C. C. PAKES. New edition, revised by A. T. NANKIVELL. 8vo., 164 pages. D. Van Nostrand & Co., New York. Price, \$1.75.

In the preface of this book, the reviser tells us that it is intended for candidates for the degree of Doctor of Public Health in Great Britain. A careful perusal of the book shows it to be very elementary in character, going into altogether too many details in the discussion of analytical methods. In this country, the book is of such a quality as would be used by high school students, and would also be of value in public libraries where very young men go to find books of a semi-popular nature. The book has the appearance of having been hastily written, and still more hastily proof-read, as is evidenced by the following errors which were noted:

Page 7: 4.55 grams instead of "parts" per one hundred thousand.

Page 56: "Redux" instead of "reflux."

Page 77: "Filter" funnel instead of "separating" funnel.

Page 92: Fixed acidity of Sherry 270 instead of 0.270.

Page 107: 100 grams is taken.

The spelling throughout the book is not altogether uniform. The author speaks of "grammes," and of milligrams and kilograms, also mixes metric, and common weights and measures, and refers the specific gravity to a basis of 1000 instead of to 1.000 as is now customary. A number of antiquated expressions, such as "Baryta water" are used.

The following errors in chemistry are especially glaring:

Page 27: In mentioning the white precipitate of lead sulfate formed on the addition of H_2SO_4 to a water containing lead, no mention is made of the fact that the presence of barium would also give a white precipitate.

Page 53: The Kjeldahl method as described would undoubtedly lead to a loss of ammonia before the distillation.

Page 84: The ashing of flour in a platinum dish is recommended.

The author apparently forgets the effect on platinum of the phosphorus present in cereals.

Page 93: In testing for arsenic, the author recommends the Reinsch test, but makes no mention of the Gutzeit test and its modifications which latter methods are quicker and more easily carried out.

The book is divided into the following divisions: Analysis of water, milk, butter, flour, bread, coffee, spirits, wines, beer, vinegar, air, soils, disinfectants, microscopy, meat inspection. There is also a chapter on reagents and standard solutions in the middle of the book, while additional directions for reagents are given in each chapter, oftentimes without mention of the solvent to be used. It would considerably improve the book if all the directions for the preparation of reagents and standard solutions were in one place, preferably in the back of the book in an appendix.

The best part of the book consists of the collection of typical water analyses with notices on their interpretation. Thirty such analyses are given and well explained.

D. D. BEROLZHEIMER

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York

- Cellulose, Chemistry of, with Special Reference to the Textile and Fibre Industries.** By C. G. SCHWALBE. Vol. II. L. 8vo., pp. 660. Price, \$7.00. Gebrüder Borntraeger, Berlin. (German.)
- Chemical Industries of Belgium, Netherlands, Norway and Sweden.** By THOMAS H. NORTON. 8vo., pp. 85. Dept. of Commerce and Labor, Special Agents Series No. 65.
- Civil Engineers' Pocketbook.** By ALBERT I. FRYE. 8vo., pp. 1658. Price, \$5.00. D. Van Nostrand Co., New York.
- Dairy Technology: Dairy Products and their Uses.** By C. LARSEN. Sm. 8vo., pp. 298. Price, \$1.50. John Wiley & Sons, New York.
- Electrical Photometry and Illumination.** By H. BOHLE. 8vo., pp. 234. Price, \$2.75. Chas. Griffin & Co., London.
- Food Inspection and Analysis.** By ALBERT E. LEACH AND ANDREW L. WINTON. 3rd Edition. L. 8vo., pp. 1001. Price, \$7.50. John Wiley & Sons, New York.
- History of Chemistry.** By JAMES CAMPBELL BROWN. Vol. II. 8vo., pp. 543. Price, \$2.75. J. & A. Churchill, London.
- Hydrocellulose, Acetylcellulose and the Determination of Acetic Acid in Acetylcelluloses.** By W. BECK. 8vo., pp. 58. Thesis, University of Leipzig, Leipzig. (German.)
- Inorganic Chemistry, Gmelin and Kraut's Handbook of.** Vol. III, Part 1. By C. FRIEDHEIM AND F. PETERS. 7th edition. L. 8vo., pp. 1568. Price, \$16.50. Carl Winter, Heidelberg. (German.)
- Iron and Steel, An Outline of the Metallurgy of.** By A. H. SEXTON AND J. S. G. PRIMROSE. 2nd edition. 8vo., pp. 586. Price, \$3.25. Scientific Publishing Co., London.
- Lead Poisoning and Lead Absorption.** By THOMAS M. LEGGE AND KENNETH W. GOADBY. 8vo., pp. 308. Price, \$3.50. Longmans, Green & Co., New York.
- Leather Dyeing and Preparing.** By M. C. LAMB. 2nd edition. L. 8vo., pp. 427. Price, \$5.25. Julius Springer, Berlin. (German. Translation.)
- Metals, The Casting of.** By E. A. SCHOTT. Lex. 8vo., pp. 285. Price, \$3.50. B. F. Voigt, Leipzig. (German.)
- Metals, Electrolytic Deposition of.** By G. BUCHNER. 8vo. Price, \$1.75. M. Krayn, Berlin. (German.)
- Metal Working, Handbook of Autogenous.** By THEO KAUTNY. 8vo., pp. 712. Price, \$4.50. Carl Marhold, Halle. (German.)
- Metals, the Rarer, The Mineralogy of.** By E. COHEN AND W. O. WOOTON. 12mo., pp. 240. Price, \$1.50. Chas. Griffin & Co., London.
- Metals, Mixed, or Metallic Alloys.** By ARTHUR H. HORN. 3rd edition. 8vo. Price, \$1.50. Macmillan Co., New York.
- Metallurgy, Treatise on.** By L. DE LAUNAY. Vol. III. 8vo. Price, \$18.00. Ch. Beranger, Paris. (French.)
- Nitrocellulose Produced from Sulfite Nitrocellulose and Straw-fiber, Use of.** By K. A. NITZELADEL. 8vo. Price, \$0.25. Dissertation, University of Dresden, Dresden. (German.)
- Organic Compounds, The Preparation of.** By E. DE B. BARNETT. 8vo., pp. 326. Price, \$2.25. A. & J. Churchill, London.
- Paper: The Testing of Wood Pulp.** By R. W. SINDALL AND W. N. BACON. 8vo. Price, \$2.50. D. Van Nostrand Co., New York.
- Peat as a Source of Power.** L. 8vo., pp. 164. Price, \$1.50. Julius Springer, Berlin. (German.)
- Petroleum: Laboratory Book of Mineral Oil Testing.** By JAS. A. HICKS. 8vo., pp. 74. Price, \$1.50. Chas. Griffin & Co., London.
- Petroleum, the Motive Power of the Future.** By W. S. TOWER AND J. ROBERTS. 8vo., pp. 254. Price, \$1.50. Hodder & Stoughton, London.
- Photochemistry, Textbook of.** By A. BENRATH. 8vo. Price, \$1.50. C. Winter, Heidelberg. (German.)
- Public Health Chemistry and Bacteriology.** By DAVID MCKAIL. 8vo., pp. 409. Price, \$2.50. William Wood & Co., New York.
- Qualitative Analyses.** By WILHELM BILTZ. 8vo., pp. 129. Price, \$1.50. Akademische Verlagsgesellschaft, Leipzig. (German.)
- Rubber.** By RUDOLF DITMAR. 8vo., pp. 140. Price, \$1.75. Julius Springer, Berlin. (German.)
- Soap-Makers' Handbook.** By WILLIAM T. BRANNT. 2nd ed. 8vo., pp. 535. Price, \$6.00. Henry Carey Baird & Co., Philadelphia.
- Sugar Industry in the Philippine Islands, Handbook on the.** By G. E. NESOM, HERBERT S. WALKER, et al. L. 8vo. Price, \$2.00. Bureau of Science, Manila.
- Thorium and its Compounds, Lecture on.** By EDMUND WHITE. 8vo., pp. 228. Edmund White, London.
- Boiler Feed Piping.** By CHARLES L. HUBBARD. *Steam*, Vol. 11, 1913, No. 1, pp. 3-9.
- Caramel.** By LAWRENCE BRIANT. *Journal of the Institute of Brewing*, Vol. 18, 1912, No. 7, pp. 673-689.
- Concrete, Influence of Temperature on.** By WARREN A. HOYT. *Engineering Record*, Vol. 67, 1913, No. 3, pp. 66-68.
- Copper, The Detection of Traces of.** By W. B. FRITZ, A. GUILLAUME AND J. R. WITROW. *Journal of the American Chemical Society*, Vol. 35, 1913, No. 2, pp. 168-173.
- Cotton Goods, Fire-Resisting.** By W. B. NANSON. *Textile American*, Vol. 19, 1913, No. 2, pp. 14-16.
- Fatty Acids.** By J. L. STREVEN. *Chemical Engineering and The Works Chemist*, Vol. 11, 1913, No. 20, pp. 319-321.
- Fuel Oil.** By VIVIAN B. LEWES. *Chemical Trade Journal*, Vol. 52, 1913, No. 1340, pp. 91-92.
- Fuel, Oil as an Emergency.** By REGINALD TRAUTSCHOLD. *Practical Engineer*, Vol. 17, 1913, No. 2, pp. 115-118.
- Hydrogen Table, A New.** By L. VANINO AND A. SCHINNER. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 7, pp. 55-56.
- Inorganic Chemistry, Recent Work in. Collective Abstract.** By JAS. LEWIS HOWE. *Journal of the American Chemical Society*, Vol. 35, 1913, No. 2, pp. 184-199.
- Iron, American Ingot, vs. Steel.** By G. F. AHLBRANDT. *Journal Cleveland Engineering Society*, Vol. 1913, No. 1.
- Iron and Steel Production, Electric Furnace Methods of.** By JOHN B. C. KERSHAW. *Chemical World*, Vol. 2, 1913, No. 2, pp. 61-64.
- Mercury, Comparison of Methods of Determination of.** By WILHELM BECKERS. *Archiv der Pharmazie*, Vol. 251, 1913, No. 1, pp. 4-7.
- Metals and Alloys, The Effect of High Temperatures on the Physical Properties of Some.** By I. M. BREGOWSKY AND L. W. SPRING. *The Valve World*, Vol. 10, 1913, No. 1, pp. 3-34.
- Oil from Seeds, The Extraction of.** By JOSEF MERZ. *Chemical Trade Journal*, Vol. 52, 1913, No. 1340, pp. 97-98.
- Ore Sampling without Machinery.** By JESSE SCOBEY. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 2, pp. 83-86.
- Paint Manufacture, The Latest Developments in.** By HENRY A. GARDNER. *Paint, Oil and Drug Review*, Vol. 55, 1913, No. 7, pp. 11-15.
- Paints, Metal, Primers for.** By HENRY A. GARDNER. *Paint, Oil and Drug Review*, Vol. 55, 1913, No. 4, pp. 10-13.
- Paper, Methods of Estimating the Quality of.** ANONYMOUS. *Paper*, Vol. 10, 1913, No. 7, pp. 15-17.
- Pigments Used by the Earlier Painters, with Some Description of the Methods of Detecting and Identifying Them.** By A. P. LAURIE. *Oil and Colour Trades Journal*, Vol. 43, 1913, No. 1, pp. 45-48.
- Reactions, Chemical, at very Low Pressures.** By IRVING LANGMUIR. *Journal of the American Chemical Society*, Vol. 35, 1913, No. 2, pp. 105-127.
- Rubber Content of Rubber Goods, Determination of the.** By PAUL GOLDBERG. *Chemiker Zeitung*, Vol. 37, 1913, No. 9, pp. 85-86.
- Sewage Purification.** By JAMES MILLAR NEIL. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 2, pp. 76-79.
- Sewage: Separation of Suspended Solids from Percolator Effluents.** By LEONARD CLEMENT. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 1, pp. 4-9.
- Sugar Laboratory Apparatus and its Use.** By R. S. NORRIS. *Louisiana Planter and Sugar Manufacturer*, Vol. 50, 1913, No. 6, pp. 93-96.
- Sulnite-Cellulose Extract, Analysis and Detection of.** By F. H. SMALL. *Journal of the American Leather Chemists' Association*, Vol. 8, 1913, No. 2, pp. 63-89.
- Temperature, Measurement of, by Electrical Means.** By CHAS. BURTON THWING. *Steam*, Vol. 11, 1913, No. 2, pp. 40-42.
- Varnish Materials, Some Colonial and Indian.** By THOMAS A. HENRY. *Oil and Colour Trades Journal*, Vol. 43, 1913, No. 744, pp. 213-216.
- Ventilation for Industrial Plants.** By CHARLES L. HUBBARD. *Steam*, Vol. 11, 1913, No. 2, pp. 33-36.
- Water Analysis, The Use of Potassium Palmate in.** By C. BLACHER, P. GRUENBERG AND M. KISSA. *Chemiker Zeitung*, Vol. 37, 1913, No. 6, pp. 56-58.
- Water from Mains, Detection and Colorimetric Determination of Lead Copper and Zinc in.** By I. W. WINKLER. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 3, pp. 38-44.
- White Lead, The Toxicity of.** By CHARLES A. LINE. *Drugs, Oils and Paints*, Vol. 28, 1913, No. 8, pp. 295 and 301-302.
- Wood Preservation.** By H. V. SCHRECK, F. M. BOND AND H. F. WEISS. *Engineering Record*, Vol. 67, 1913, No. 4, pp. 108-110.

RECENT JOURNAL ARTICLES

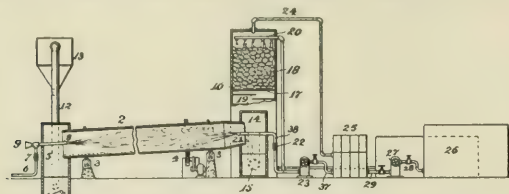
- Arsenic, Quantitative Determination of.** By F. LEHMANN. *Archiv der Pharmazie*, Vol. 251, 1913, No. 1, pp. 1-4.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Suspensible Sulfur. H. W. Hillyer, Dec. 24, 1912. U. S. Pat. 1,048,161. The patentee claims the invention of a new form of sulfur which he terms suspensible sulfur, the material being suspensible in water and which, when so suspended, is not coagulable by sulfuric acid. The product is to be used as a fungicide.

Recovery of Sulfuric Acid and Iron from Ferrous-Sulfate Sludge. C. A. Weeks, Dec. 24, 1912. U. S. Pat. 1,048,247. In the patentee's preferred process, concentrated ferrous sulfate solution is sprayed into the upper end of a heated, slightly inclined, rotating, tubular furnace, heated by a jet of gas admitted to the lower end of the furnace. The ferrous sulfate is gradually heated within the furnace until the greatest temperature zone is reached, at which the calcination of the ferrous sulfate crystals takes place with the result that ferric



oxid is formed and the whole content of sulfur gases with other vapors are released. The ferric oxid is discharged from the lower end of the furnace, while the sulfur gases and other vapors pass from the higher end of the furnace where the temperature zone is cool and are delivered into the condensing tower where it is subjected to treatment of a spray of weak solution of sulfuric acid. This condenses and absorbs the contained sulfuric acid gas, the other gas passing on. The absorbed sulfuric acid gas is withdrawn from the condensing tower and stored or used over again; the ferric oxid is collected from the lower end of the furnace, cooled and recovered as ferric oxid free from sulfur.

Formic Acid. W. H. Walker, Dec. 31, 1912. U. S. Pat. 1,048,609. In making formic acid by the reaction of sulfuric acid on a formate, the patentee uses a formate substantially free from water whereby the reaction proceeds without injurious rise of temperature or substantial loss* of formic acid.

Waterproofing Concrete. A. C. Horn, Dec. 31, 1912. U. S. Pat. 1,048,695. The composition comprises Chinese wood oil, calcium stearate and casein, and a preservative compound.

Electric-Furnace Lining. Frederick M. Becket, Jan. 7, 1913. U. S. Pat. 1,049,801. The lining consists of a refractory material having an adherent facing of ferrotungsten reduced from the refractory material.

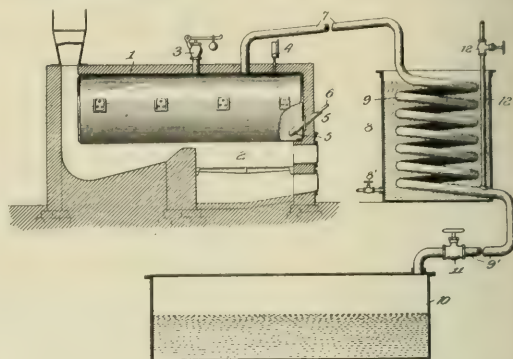
Luminous or Flaming Arc Electrode. Joseph L. R. Hayden, Jan. 7, 1913. U. S. Pat. 1,049,854. The electrode contains titanium carbide and cerium titano-fluoride.

Tar-Paint Manufacture. Friedrich Raschig, Jan. 7, 1913. U. S. Pat. 1,049,916. The paint consists of an emulsion of tar, clay and water, produced by mixing clay with water and then gradually stirring tar and water into the mixture until the tar is uniformly distributed.

Purifying Asbestos. W. C. Arsem, Jan. 7, 1913. U. S. Pat. 1,049,972. Difficultly removable iron oxid is removed from asbestos by soaking the crude material in a 50% solution of

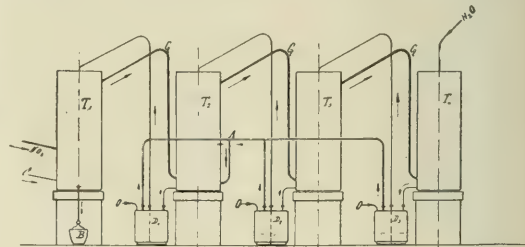
orthophosphoric acid for from 24 to 72 hours and washing the fibers to remove the adherent acid.

Gasoline Manufacture. W. M. Burton, Jan. 7, 1913. U. S. Pat. 1,049,667. On distilling at from 650°-850° F. the volatile constituents of the liquid portions of the paraffin series of petroleum distillations having a boiling point upward of 500° F.,



low-boiling products of the same series are obtained, by maintaining a pressure of 4 to 6 atmospheres on the vapors throughout their course from the still through the condenser and while undergoing condensation. From time to time the accumulations of gas from the products of condensation are released.

Nitric Acid. Moest and von Berneck, Jan. 7, 1913. U. S. Pat. 1,049,754. In the production of concentrated nitric acid gases it has been found that a more concentrated nitric acid is obtained if oxygen is used instead of atmospheric air for converting these gases into nitric acid in the presence of water.



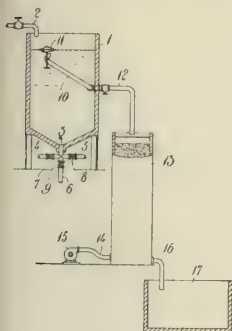
The patentee charges with oxygen the apparatus serving for the conveyance of the liquid in the absorption system and reintroduces the oxygen leaving the apparatus simultaneously with the entrained vapors containing the nitric acid.

Non-Inflammable Cellulose Compound. W. G. Lindsay, Jan. 7, 1913. U. S. Pat. 1,050,065. The composition contains 100 parts of acetyl cellulose, from 10 to 20 parts of triphenylphosphate and from 1 to 2 parts of urea in admixture with acetylenetetraclorid and acetone.

Concentrated Nitric Acid. Moest and von Berneck, Jan. 14, 1913. U. S. Pat. 1,050,160. The patentees produce concentrated nitric acid in a direct way by treating dilute nitric acid with a mixture of nitrogen peroxid and oxygen. The mixture is subjected to the action of oxygen to expel the non-oxidized nitric oxid gases from the nitric acid.

Separating Copper from Other Metals. T. A. Edison, Jan. 14, 1913. U. S. Pat. 1,050,629 and 30. In separating metallic copper from other metals the associated metals are treated with a solution of ammonium sulfate or copper sulfate containing a reducible haloid of a metal of variable valence and supplying an oxygen-containing gas to the mixture.

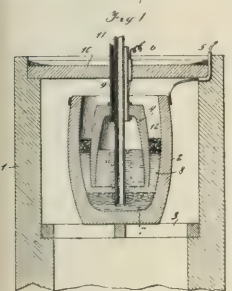
Alcohol from Sulfite Liquor. P. B. Ekström, Jan. 14, 1913. U. S. Pat. 1,050,723. In the process of manufacturing alcohol



by fermenting the saccharine matters of sulfite liquor from sulfite pulp, it is difficult to maintain a quantity of free oxygen sufficient for the development of the yeast, due to the fact that the liquor contains reducing compounds, or compounds which are easily oxidized during the fermentation, that rapidly consume the free oxygen that may be supplied by usual aeration.

The patentee's process consists in adding to the liquor before fermenting the same, a catalyzer for oxidation and then aerating the liquor. The catalyzer effects a rapid oxidation of those compounds which later on during the fermentation process would be capable of consuming the free oxygen in the liquor.

Economic Method of Obtaining Gases. C. E. Acker, Jan. 21, 1913. U. S. Pat. 1,050,902. This is a process of continuously separating gases from gaseous mixtures or from liquids or solids



containing them and is adapted for the production of nitrogen from atmospheric air as well as the production of hydrogen through the decomposition of steam or water.

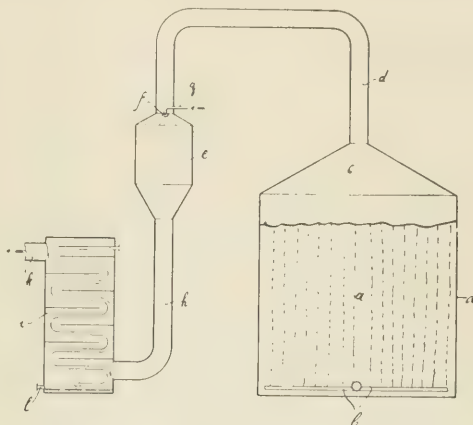
In the production of nitrogen from atmospheric air, such air is brought into contact with a heated metal capable of being oxidized, such as lead. A metal oxid is formed and the nitrogenous residue separated therefrom. The metal oxid is dissolved in a menstruum preferably consisting of a mixture of

fused alkali metal salts, and the metal oxid is reacted upon by a reducing agent which is held in solution in such menstruum. The process may be continuously carried out in the apparatus illustrated.

Potash, Iodine and Chlorine from Seaweeds. Cameron and Moore, Feb. 4, 1913. U. S. Pat. 1,051,984. The filtered and partially evaporated solution obtained by lixiviating the ash of seaweeds is electrolyzed in a cell having its anode and cathode chambers separated by a diaphragm, thus oxidizing the liberated iodine to iodic acid. By treating the anode solution with ferrous sulfate (or iron) and sulfuric acid, the iodine is separated from the iodic acid. Potassium hydroxide is found in the cathode solution.

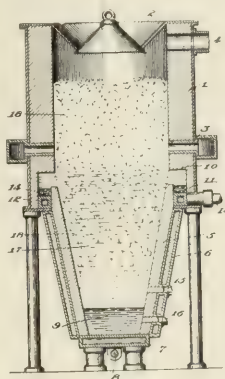
Regaining Alcohol from Air Passed through Fermenting Vats. A. Zeckendorf, Jan. 21, 1913. U. S. Pat. 1,051,051. The more recent fermentation processes in which a large quantity of

air is caused to pass through the fermenting mash it has heretofore not been possible in all cases to economically separate the alcohol absorbed. The patentee adds to the mixture of alcohol



and air a vapor, such as steam; this is quickly taken up by the mixture of alcohol and air and has every opportunity to absorb the alcohol. Since the water can be more easily removed from air than alcohol, the absorbed alcohol—with the exception of but small traces—can now be separated from the air by simply condensing the vapor. The alcohol is therefore nearly entirely regained.

Ferrosilicon by Reduction. E. A. Byrnes, Jan. 21, 1913. U. S. Pat. 1,051,194. According to this process, refractory metal-bearing ores and compounds and specifically a charge consisting



of a silicon compound, a source of iron and coal for the production of ferrosilicon, are reduced by submerging the lower portion of the charge in a vertical molten resistor-column, preheating the unsubmerged upper portion by passing air and hot products of combustion upward through it, and heating the submerged lower portion by passing through the molten resistor an electric current of energy-density increasing downward toward the zone of reduction. The electric terminals are preferably of molten ferrosilicon, one being a ring surrounding the upper end of the resistor-column and the other a body of

the metallic product beneath the lower end of this column. As reduction proceeds the excess slag and metal are tapped out and additions are made to the charge.

Acetone and Higher Alcohols by Fermentation of Starch Sugars and Other Carbohydrate Materials. A. Fernbach and E. H. Strange, Nov. 12, 1912. U. S. Pat. 1,044,368. In this process carbohydrate matter is mixed with water, and a suitably degraded yeast added. The mixture is then sterilized, a ferment of the type of the butylic bacillus of Fitz added and the mixture fermented in the absence of air.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF FEBRUARY, 1913

ORGANIC CHEMICALS

Acetanilid.....	Lb.	21	@	23
Acetic Acid (28 per cent.).....	C.	2.00	@	2.15
Acetone (drums).....	Lb.	16 ¹ / ₂	@	17 ¹ / ₂
Alcohol, grain (188 proof).....	Gal.	2.55	@	2.57
Alcohol, wood (95 per cent.).....	Gal.	.50	@	.52
Alcohol, denatured (180 proof).....	Gal.	.40	@	.42
Amyl Acetate.....	Gal.	2.35	@	2.55
Aniline Oil.....	Lb.	10 ¹ / ₂	@	10 ⁵ / ₈
Benzoic Acid.....	Lb.	.23	@	.27
Carbon Tetrachloride (drums).....	Lb.	8 ¹ / ₂	@	.9
Carbon Bisulfide.....	Lb.	6 ¹ / ₂	@	.8
Chloroform.....	Lb.	.25	@	.35
Carbolic Acid (drums).....	Lb.	.14	@	.15
Citric Acid (domestic), crystals.....	Lb.	.40	@	40 ¹ / ₂
Camphor (refined in bulk).....	Lb.	42 ¹ / ₂	@	.44
Dextrine (imported potato).....	Lb.	.6	@	.7
Dextrine (corn).....	C.	2.60	@	2.81
Ether (U. S. P., 1900).....	Lb.	.14	@	.20
Formaldehyde.....	Lb.	8 ¹ / ₂	@	9 ¹ / ₂
Glycerine (dynamite).....	Lb.	18 ¹ / ₂	@	.19
Oxalic Acid.....	Lb.	7 ⁷ / ₈	@	8 ¹ / ₈
Pyrogallie Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	.29	@	.31
Starch (corn).....	C.	1.82	@	2.27
Starch (potato).....	Lb.	5 ¹ / ₄	@	5 ³ / ₄
Tannic Acid (commercial).....	Lb.	.35	@	35 ¹ / ₂
Tartaric Acid, crystals.....	Lb.	30 ¹ / ₄	@	.31

INORGANIC CHEMICALS

Acetate of Lime (gray).....	C.	2.50	@	2.60
Acetate of Lead (brown, broken).....	Lb.	7 ³ / ₄	@	.8
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate.....	C.	.90	@	1.75
Ammonium Carbonate, domestic.....	Lb.	.8	@	8 ¹ / ₂
Ammonium Chloride, gray.....	Lb.	6 ¹ / ₂	@	6 ¹ / ₂
Aqua Ammonia (drums) 16°.....	Lb.	2 ¹ / ₄	@	2 ¹ / ₂
Arsenic, white.....	Lb.	4 ¹ / ₂	@	.5
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Barium Chloride.....	C.	1.70	@	1.80
Barium Nitrate.....	Lb.	.5	@	5 ¹ / ₄
Borax, crystals (bags).....	Lb.	3 ³ / ₄	@	4 ¹ / ₄
Boric Acid, crystals (powd.).....	Lb.	.7	@	7 ¹ / ₂
Bromine, bulk.....	Lb.	.30	@	.35
Bleaching Powder (35 per cent.).....	C.	1 ³ / ₈	@	1 ¹ / ₂
Barytes (prime white, foreign).....	Ton	18.50	@	22.50
Blue Vitriol.....	Lb.	5 ¹ / ₄	@	5 ¹ / ₂
Calcium Chloride.....	C.	.65	@	.90
Chalk (light precipitated).....	Lb.	.4	@	.5
China Clay (imported).....	Ton	11.50	@	18.00
Feldspar.....	Ton	7.00	@	9.00
Fuller's Earth, powdered.....	C.	.80	@	.85
Green Vitriol (bulk).....	C.	.55	@	.60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.05	@	3.10
Lead Nitrate.....	Lb.	8 ¹ / ₈	@	8 ¹ / ₄
Lithium Carbonate.....	Lb.	.65	@	.70
Magnesite (raw).....	Ton	7.50	@	8.50
Nitric Acid, 36°.....	Lb.	3 ³ / ₈	@	4 ¹ / ₄
Phosphorus.....	Lb.	.35	@	.90
Phosphoric Acid, sp. gr. 1.75.....	Lb.	21 ¹ / ₂	@	25 ¹ / ₂
Plaster of Paris.....	Hbl.	1.50	@	1.70
Potassium Bromide.....	Lb.	.39	@	.40
Potassium Permanganate (bulk).....	Lb.	9 ³ / ₄	@	.11
Potassium Cyanide (bulk) 98-99%.....	Lb.	.19	@	.24
Potassium Iodide (bulk).....	Lb.	2.60	@	2.65
Potassium Chlorate, crystals.....	Lb.	.9	@	10 ¹ / ₂
Potassium Nitrate (crude).....	Lb.	4 ³ / ₄	@	.5
Potassium Bichromate, 50°.....	Lb.	6 ¹ / ₈	@	.7

Quicksilver, Flask.....		40.00	@	—
Salt Cake (glass makers').....	C.	.55	@	.65
Silver Nitrate.....	Oz.	39 ³ / ₈	@	.40
Soapstone in bags.....	Ton	10.00	@	12.00
Sodium Acetate.....	Lb.	.4	@	4 ¹ / ₂
Sodium Chlorate.....	Lb.	8 ¹ / ₄	@	9 ¹ / ₂
Sodium Bicarbonate (English).....	Lb.	2 ³ / ₄	@	.3
Sodium Bichromate.....	Lb.	.5	@	5 ¹ / ₂
Sodium Hydroxide, 60 per cent.....	C.	1.60	@	1.65
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot.....	C.	2.62 ¹ / ₂	@	.65
Sodium Silicate (liquid).....	C.	.65	@	1.50
Strontium Nitrate.....	Lb.	6 ⁷ / ₈	@	7 ⁵ / ₈
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfuric Acid, 60° B.....	C.	.85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	.75	@	.80
Tin Bichloride (50°).....	Lb.	14 ¹ / ₄	@	14 ¹ / ₂
Tin Oxide.....	Lb.	.52	@	.54
Zinc Chloride (granulated).....	Lb.	4 ¹ / ₂	@	.5
Zinc Sulfate.....	Lb.	2 ¹ / ₄	@	2 ¹ / ₂

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	.42	@	.45
Black Mineral Oil, 29 gravity.....	Gal.	13 ¹ / ₂	@	.14
Castor Oil (No. 3).....	Lb.	9 ¹ / ₂	@	10 ¹ / ₂
Ceresin (yellow).....	Lb.	.12	@	.22
Corn Oil.....	C.	5.80	@	5.85
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	.39	@	39 ¹ / ₂
Cylinder Oil (light, filtered).....	Gal.	21 ¹ / ₂	@	.32
Japan Wax.....	Lb.	9 ³ / ₄	@	.10
Lard Oil (prime winter).....	Gal.	.88	@	.92
Linseed Oil (double-boiled).....	Gal.	.50	@	.52
Paraffine Oil (high viscosity).....	Gal.	.26	@	.28
Paraffine (crude 120 & 122 m. p.).....	Lb.	3 ¹ / ₂	@	3 ³ / ₄
Rosin Oil (first run).....	Gal.	.34	@	.36
Spindle Oil, No. 200.....	Gal.	.18	@	.19
Sperm Oil (bleached winter), 38°.....	Gal.	.72	@	.74
Stearic Acid (double-pressed).....	Lb.	9 ³ / ₈	@	.10
Tallow (acidless).....	Gal.	.64	@	.67
Tar Oil (distilled).....	Gal.	.30	@	.31

METALS

Aluminum (No. 1 ingots).....	Lb.	25 ¹ / ₂	@	.26
Antimony (Hallet's).....	Lb.	.9	@	9 ¹ / ₂
Bismuth (New York).....	Lb.	2.10	@	2.15
Copper (electrolytic).....	Lb.	14 ¹ / ₂	@	.15
Copper (lake).....	Lb.	14 ⁷ / ₈	@	.15
Lead, N. Y.....	Lb.	4.30	@	4.40
Nickel.....	Lb.	.50	@	.55
Platinum (refined).....	Oz.	46.00	@	—
Silver.....	Oz.	.62	@	—
Tin.....	Lb.	.49	@	.50
Zinc.....	Lb.	6.35	@	6 ¹ / ₂

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	3.25	@	—
Fish Scrap, domestic, dried.....	Unit	nominal	@	—
Blood, dried.....	Unit	2.80	@	—
Tankage, high-grade.....	Unit	2.70	@	.10
Bone, 4 ¹ / ₂ and 50, ground, raw.....	Ton	28.00	@	—
Potassium, "muriate," basis 80%.....	Ton	38.55	@	—
Phosphate, acid, 16 per cent.....	Ton	7.00	@	8.00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	3.00	@	3.25
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Pyrites, furnace size, imported.....	Unit	0.13 ¹ / ₂	@	—
Castor meal.....	Unit	3.10	@	—
Mowrah meal.....	Ton	9.00	@	—

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

APRIL, 1913

No. 4

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, Wm. McMurtrie, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly.

Foreign postage, seventy-five cents. Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

No claims will be allowed unless made within 60 days

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

The Nichols-Hesse Dinner	268
The Research Bureau of the Chemists' Club	268
Negative Cooperation	269

ORIGINAL PAPERS:

Accuracy and Limitations of Coal Analysis. By A. C. Fieldner	270
The Effect of Certain Pigments on Linseed Oil; with a Note on the Manganese Content of Raw Linseed Oil. By E. W. Boughton	282
Pine Nut Oil. By Maxwell Adams and August Holmes	285
Analyses of Certain of the Pacific Coast Kelps. By E. G. Parker and J. R. Lindemuth	287
The Specific Heat of Coal and its Relation to the Presence of Combined Water in the Coal Substance. By Horace C. Porter and Guy B. Taylor	289
Application of the Dimethyl Sulfate Test for Determining Small Amounts of Petroleum or Asphalt Products in Tars. By Charles S. Reeve and Richard H. Lewis	293
The Determination of Oxygen in Metallic Tungsten Powder and some Notes on the Determination of Oxygen in Steel. By Charles Morris Johnson	295
The Determination of Phosphorus in Ferro-Tungsten, Metallic Tungsten Powder, Tungsten Oxide and Tungstic Acid by Direct Solution. By C. M. Johnson	297
A Colorimetric Method for the Determination of Chromium in Steel. By Frank Garratt	298
Waters of the Breitenbush Hot Springs, Oregon. By Walton Van Winkle	300
Phosphates in Surface Waters. By George S. Jamieson	301
The Determination of Zinc in Ores. By D. J. Demorest	302
A Polarimetric Method for the Determination of Starch in Paper. By Christian E. G. Porst and Harry A. Crown	304

LABORATORY AND PLANT:

Chemical Engineering and the New Laboratories at Columbia University. By M. C. Whitaker and R. K. Murphy	304
Technical Accounting and Chemical Control in Sugar Manufacture. By David L. Davoll, Jr.	313
Sterilization of Water Supply at Trenton. By H. C. Hottel	319
The Determination of Mineral Aggregate in Bitumen Pavements. By C. C. O'Loughlin	320

ADDRESSES:

The Problem of International Congresses of Applied Chemistry. By Bernhard C. Hesse	321
--	-----

The Production of Synthetic Ammonia. By F. Haber and R. Le Rossignol	328
Cheaper Alumina and Aluminum from Mineral Silicates. By Alfred H. Cowles	331
The Serpek Process for the Manufacture of Aluminium Nitride. By J. W. Richards	335

CURRENT INDUSTRIAL NEWS:

Sulfur Mining in Texas	337
New Uses for Naphthalene	337
New Departures in Aluminum Plate	337
The Paper Industry of Norway and Sweden	337
1912 Statistics for Germany	337
Potash from Seaweed in Mexico	338
Potash from Feldspar	338
The Present Status of the Thiogen Process	338
The Iodine Industry	339
The Manufacture of Gas Mantles	339
On Some Developments in the Mineral Oil Industry	339
The World's Petroleum Output in 1912	340
The Progress of Papermaking in 1912	340
A Record of Industrial Growth	340
The Lecithin and Albumin Industry	340
Hot Water Supply Systems to Minimize Corrosion	341

SCIENTIFIC SOCIETIES:

American Chemical Society—Forty-Seventh Meeting at Milwaukee. Program of Papers	342
Standard Sample of Phosphate Rock	344
American Electrochemical Society—Twenty-Third General Meeting	344
The Report of the Secretary of the Eighth International Congress of Applied Chemistry	344
Final Shipment of Eighth International Congress Reports, Volumes 25-29	348

NOTES AND CORRESPONDENCE:

An Application of the Electric Resistance Furnace to the Determination of Oxygen in Iron and Steel—A Criticism	349
An Accurate Viscosimeter with Practical Qualities	349
Court Decision on the Manufacture of Carborundum	350
New Geological Survey Building Provided	350
Potash Lands Withdrawn	350
The Rare Earth Minerals	350

BOOK REVIEWS:

Chloride of Lime in Sanitation: Water, Its Purification and Use in the Industries; The Chemical Analysis of Lead and its Compounds	350
--	-----

NEW PUBLICATIONS:

RECENT INVENTIONS	352
MARKET REPORT	354

EDITORIALS

THE NICHOLS-HESSE DINNER

The chemists of America, in whose behalf Dr. William H. Nichols, as president, and Dr. Bernhard C. Hesse, as secretary, assumed the burden of organizing and administering the affairs of the Eighth International Congress of Applied Chemistry, will celebrate the successful completion of this gigantic undertaking by a Nichols-Hesse dinner. Dr. Edward W. Morley, the faithful honorary president of the Congress, will preside at the function which will include not only a dinner but the presentation to the guests of testimonials of regard and appreciation.

The committee, made up of representatives of the American Chemical Society, American Electrochemical Society, American Institute of Chemical Engineers, Chemists' Club, American Sections of the Society of Chemical Industry and the New York Section of the Verein Deutscher Chemiker, will make this a memorable event as the closing chapter of the Eighth Congress. It is distinctly a chemists' function and will, therefore, be given at the Chemists' Club. The date selected is April 19th, and tickets may be obtained from Dr. L. H. Baekeland, of Yonkers, New York.

The Eighth Congress was the most important event in the history of Applied Chemistry in America. Our professional progress and our industries were opened to the critical inspection of picked representatives from all important foreign countries. The assumption of the responsibilities for the organization and administration of this great task took courage and foresight, and involved a most extraordinary amount of hard work and anxiety, so that its successful completion calls for the admiring gratitude of every American chemist. What was done was undertaken solely in the interest of Applied Chemistry and its followers and without regard to society or business affiliations. This celebration, therefore, becomes not a matter of this organization or that, but a sincere tribute of appreciation from American chemists in general to the men who assumed and carried our burden so successfully.

Many willing chemists will not be able to come to the dinner, but will have to rely on letters and telegrams to express their appreciation. Whatever method may be dictated by conditions, sincere and cordial admiration and applause will be general among American Chemists for the magnificent Nichols-Hesse team-work.

THE RESEARCH BUREAU OF THE CHEMISTS' CLUB

On February 22nd the Library Committee of the Chemists' Club announced the organization of a Research Bureau. The Chemists' Club Library has the largest collection of chemical literature in America. Donations by Charles F. Chandler, Morris Loeb, the American Chemical Society, the Society of Chemical

Industry, J. W. Mallet, Herman Frasch and many others have made it possible to assemble complete up-to-date editions of practically all the important scientific and technical chemical publications, both American and foreign. Notable examples of unusually valuable possessions are the following:

American Chemical Journal, 1879 to date.
American Journal of Science, 1819 to date.
Analyst, 1877 to date.
Berichte der deutschen chemischen Gesellschaft, 1868 to date.
Bulletin de la Société Chimique, 1861 to date.
Bureau of Chemistry Bulletins, 1-160, 1882 to date.
Canadian Patent Office Record, 1890 to date.
Chemical News, 1867 to date.
Chemiker Zeitung, 1877 to date.
Comptes Rendus, 1835 to date.
Encyclopedie Chimique-Fremy's, complete.
Experiment Station Bulletins 1-248, 1889 to date.
Experiment Station Record, 1889 to date.
Gazzetta chimica italiana, 1871 to date.
Illustrated Official Journal (British Patents), 1900 to date.
International Sugar Journal and its predecessor, Sugar Cane, 1872 to date.
Journal für praktische Chemie, 1828 to date.
Journal of the American Chemical Society, 1879 to date.
Journal of the Association of Engineering Societies, 1881 to date.
Journal of the Chemical Society, London, Abstracts and Transactions, 1849 to date.
Journal of the Society of Chemical Industry, 1882 to date.
Liebig's Jahresberichte, 1847 to date.
Pharmaceutical Journal, 1841 to date.
Proceedings of the American Pharmaceutical Association, 1857 to date.
Repertorium der Technischen Journal Literature, 1829 to date.
School of Mines Quarterly, 1879 to date.
Transactions of the American Institute of Mining Engineers, 1871 to date.
U. S. Patent Office Gazette, 1790 to date.
Wagner's Jahresberichte, 1855 to date.
Zeitschrift für analytische Chemie, 1862 to date.
Zeitschrift für angewandte Chemie, 1887 to date.
Zeitschrift für anorganische Chemie, 1889 to date.
Zeitschrift für Untersuchung der Nahrungs und Genussmittel and its predecessor, 1881 to date.

When the Morris Loeb Library has been entirely moved in, the Chemisches Zentralblatt, 1830 to date, and Liebig's Annalen complete, 1826 to date, will be added to the above list as well as all of the important English, French and German publications on purely theoretical and physical chemistry.

The Charles Frederick Chandler Library, the most complete private technical library in the United States is only partly installed.

Information on any chemical subject that has been investigated and put into print can now be supplied at reasonable cost to busy professional men, technical publications, lawyers, patent attorneys, manufacturers and teachers. On short notice articles will be copied, translations made, bibliographies prepared and searches of chemical or patent literature carried on, both in the Chemists' Club Library and in the principal libraries of New York City. The world's work in chemistry is thus made available to all.

While the Chemists' Club Library is making every effort to obtain all the most valuable chemical textbooks and treatises and possesses a great many of them, it realizes that its greatest service to chemical progress is to be rendered by means of the scientific and technical journals that contain original articles and reports. Every chemist owns the best books on his particular branch of the subject but it is absolutely impossible for him to possess complete editions of the multitude of valuable journals now being printed or to obtain the back numbers he needs when he needs them. At the same time the various branches of chemistry are so intimately connected, interwoven and dependent upon each other that in research of any sort it is practically always necessary to cover the whole field in order to find out what has been done as well as to prevent duplication of work. Only such facilities as are now offered by the Research Bureau of the Chemists' Club can supply the needs of modern chemical investigation and progress.

In addition to the Research Bureau, Club members, resident and non-resident, have access to the Circulating Library, on payment of handling charges. Eight thousand duplicates of books, pamphlets, reprints, etc., are available for study and use by any member in the reach of mail or express service. Many triplicates are also on hand to be exchanged for desirable literature or sold to those who need them for the completion of personal files.

In return for the many advantages now offered by the Chemists' Club, every chemist in America owes it his most hearty support. Any books, reprints, or journals in odd numbers, volumes or broken sets can be used by it with unusual and often surprising results. Odd, old volumes and particular editions are of the utmost importance in patent and research work, as well as for completing sets that are in many cases useless if incomplete.

The Chemists' Club believes in the spread of chemical knowledge and understanding. It knows that modern chemistry can no longer depend upon accidental discoveries for progress. It offers ample material for intelligent and productive research. May the American Chemists use abundantly these new resources and justify the patience and faith of those who have labored so long to make possible this remarkable expansion of the work of the Chemists' Club!

NEGATIVE COÖPERATION

Speakers who pretend to keep up with the latest

styles in matters of thought transmission sooner or later work their theme around to "Efficiency" or "Coöperation." Men trying to accomplish something worth while often find the conviction gaining on them that both of these words are "happy thoughts" but are a long way from tangible realities. People are daily becoming more reluctant to undertake public work, not because they are unwilling to sacrifice their time, ability and money for the good of others, but because they are met at the outset with a condition which for want of a better term we shall call "negative coöperation." Men of energy and ability are often elevated to positions of honor and trust and are pelted by their friends with bouquets only to find that the bouquets are sooner or later displaced by bricks. Others hesitate to accept political responsibility because they know that the blatant unreasoning criticism of the yellow press is inevitable.

Why do we not practice coöperation as well as preach it? Why do we select a most able mechanic to erect a structure of great importance to us and then give him a kit of tools containing saws, hammers and chisels made of rubber? Is it not enough to ride on the wagon we have delegated one of our fellow workers to draw for us without letting our own feet drag?

This issue of the Journal contains the final report of the Secretary of the Eighth International Congress and also an address by Dr. Hesse, drawing some striking lessons and offering suggestions which should be of inestimable value to future organizations. Some vivid examples of negative coöperation are disclosed in these records.

Early in May, 1912, definite arrangements between the officers of the Congress and the printers were completed, in which it was provided that all copy received before July 16th should be made up into 4000 sets of 24 volumes, or a total of 96,000 volumes, and delivered at the Columbia University Gymnasium before the Congress opened. The printers fully lived up to that agreement. They further agreed to give the subsequent printed matter of the Congress the right of way over everything else in their office (provided copy was completely delivered by the close of September) and to have all such matter printed and bound by November 15, 1912.

It became perfectly clear in September that the necessary coöperation on the part of lecturers, participants in discussions and contributing authors for complete delivery of copy according to agreement, would not be forthcoming. Therefore, the right-of-way arrangement with the printer had to be cancelled in order to avoid unnecessary financial loss. Not until March 11, 1913, was it possible to get from the authors all of the copy of what is now Volumes 25, 26, 27 and 28—this in spite of repeated and most urgent letters from the Secretary asking for that material. The printer was then under contract with others and the Congress matter had to take its place in line, with consequent additional delay. Even now many of those whose formal remarks or other communications should be embodied in these volumes are not represented. Had these volumes been sent to press in September with only

the material then available, they would have been very meagre and some of the most important papers would not have appeared.

The Congress had placed December 31, 1912, as its delivery date, counting with absolute confidence upon the coöperation of its own members, and for this delay the delinquent members of this Congress are alone to blame. The Congress and the printers were ready to perform their part, but they were not given any chance because the prompt coöperation they needed, and had every right to expect, had been withheld.

The fact that some of the members of the Congress will be unable to get copies of Volumes 1-24 is also due to another case of negative coöperation. In March, 1911, and in almost every one of the succeeding Congress publications, as well as in the various technical journals, attention was directed to the fact that memberships completed after July 1st could not be guaranteed the full reports. It is perfectly obvious to anyone that full information in regard to the demand was needed by the officers in order to provide the necessary number of volumes. As it was, the contracts for paper and printing had to be made when the total membership was only 1200—that after five

months' active campaigning for members. Four thousand sets were then ordered with the provision that this number could be increased up to 7500 at any time prior to July 16th. Renewed efforts to obtain members were made, but at the end of ten weeks when the time limit for extension expired, the membership had risen to only 1800. Therefore, with a surplus of almost 2000 sets, it was not regarded as essential to increase the financial burden by adding to the original contract. The Congress is now, when it is too late to remedy matters, confronted with a membership far in excess of the number of sets of its proceedings available for distribution. They will be obliged to exercise the only logical course left open to them and that is to distribute all sets now in hand in order of the dates of the memberships. Will the men who were dragging their feet in the sand while the officers of the Congress pulled hard at the wagon, assume any of the responsibility for this situation?

A high and prominent place among the world's seven wonders should be given to that human quality which impels men such as Hesse to give their time and energy to a general cause when they know that by far the greater portion of what they contribute will be absorbed to offset the indifference and negative coöperation of those for whom they work.

ORIGINAL PAPERS

ACCURACY AND LIMITATIONS OF COAL ANALYSIS¹

By A. C. FIELDNER

Received January 22, 1913

INTRODUCTION

In recent years chemical and physical tests have come into use in connection with the mining and utilization of coal. Within certain limits these tests are useful not only in establishing the fuel value but in directing the coal into the proper market for which it is best adapted, and of maintaining the standard of the output to meet the requirements of this market. The growing practice of buying on specifications demands accuracy and strict uniformity in the methods of sampling and analysis. Chemists who make only occasional analyses of coal do not as a rule realize the empirical nature of the proximate analysis, and while they may obtain concordant results as far as their own laboratories are concerned, their results may not agree with those obtained in another laboratory. These discrepancies, which are more likely to occur in some determinations like that of volatile matter or of fixed carbon, tend to discredit the whole analysis in the eyes of engineers not familiar with the difficulties peculiar to each individual determination. The object of this paper is to call attention to the fact that some constituents may be determined much more accurately than others, and to present some experimental data bearing on the probable variations that may occur in good laboratory practice.

NATURE OF COAL

Coal is used principally for fuel purposes; hence its value, other things being equal, is proportional to its calorific power. The different kinds of coal, however, vary greatly in character, so much so that each has its own particular field of usefulness. For instance, a Pittsburgh steam coal cannot be burned efficiently in an anthracite furnace, nor can a coal high in sulfur or phosphorus be used for the manufacture of foundry coke. Certain other tests, then, are also required, and for this purpose we have the conventional proximate analysis and sulfur or phosphorus determinations. While these tests may be sufficient for most industrial purposes, it is desirable at times to know the elementary composition of the coal as shown in an ultimate analysis, and its clinkering properties as indicated in the relative fusibility of the ash. No doubt other tests more suitable for individual purposes will come into use as the chemist learns what coal really is.

It is generally conceded by geologists that coal has its origin in vegetable matter that was accumulated and buried in past geological ages. Several different theories have been advanced as to the exact manner of accumulation and the particular kinds of vegetation or vegetable products that were involved. At any rate, this accumulation became more or less altered and concentrated under swampy conditions and finally buried under a load of sediments, to be subjected to a further change by the action of heat and pressure. In more or less intimate mixture with

¹ Paper read before American Coal Mining Institute, Pittsburgh, Pa., Dec. 19, 1912, by permission of the Director, U. S. Bureau of Mines.

these organic remains was deposited silt, sand, clay, and other earthy materials. Sometimes layers of sediments were laid down between the coal-forming vegetation. It is not surprising, then, that the present chemical constitution of coal is not only of an extremely complex nature but that it varies from one bed to another.

For fuel purposes the constituents of coal may be grouped into the following three classes:

1. Water or moisture.
2. The mineral impurities which remain in a somewhat altered condition, as ash on burning the coal.
3. The organic or combustible matter, which like the original vegetable matter is composed mainly of the elements carbon, hydrogen, oxygen, and nitrogen.

MOISTURE

Moisture may be accurately determined in an inorganic substance like iron ore by drying the material at a temperature slightly above the boiling point of water and noting the loss in weight. The same method when applied to coal is complicated by the oxidizing tendencies of the organic compounds, and the possibility of loss of some water of composition at the temperature of drying. The present methods of analytical chemistry do not distinguish with certainty between added moisture or water that is simply absorbed by the coal particles, and water that may be in some unstable chemical combination in the coal substance. The usual method of drying a pulverized sample for one hour at 105° C. (221° F.) is, therefore, somewhat arbitrary, and to secure uniform results a strict adherence to a standard method of procedure is necessary.

In the Bureau of Mines method¹ the moisture is determined in two stages: (1) The coarse sample received by the laboratory is pulverized to 1/4 inch size and then air-dried at 30°–35° C. (86°–95° F.). The loss in weight, which is called the air-drying loss, includes all the superficial moisture and a large portion of the loosely retained moisture. (2) The air-dried sample is then pulverized in a closed ball mill to avoid loss of moisture, mixed and sampled down to a small, powdered sample in which the residual moisture is determined by heating 1 gram for 1 hour at 105° C. (221° F.) in an oven through which dry air is being circulated. By this method duplicate results in the same powdered sample seldom vary more than 0.15 per cent.

ASH

Ash is the incombustible residue left on burning coal. It is derived from the mineral impurities in the coal and is largely composed of silica, alumina, lime, and iron compounds, together with smaller quantities of magnesia, titanium, and alkali compounds. The silica, alumina and titanium are derived from sand, clay, shale and slate; the iron oxide mainly from iron pyrites; and the lime and magnesia from their corresponding carbonates and sulfates.

The ash-forming constituents of coal may be classified in two groups:

1. Mineral matter present in an intimate mixture with the coal substance, derived either from the vegetable structure or from earthy matter intermixed as silt during the process of coal formation.

2. Mineral matter occurring in the form of thin bands and nodules of shale, bone, and pyrites; in this class are also the fragments of roof and floor that become mixed with the coal in mining.

Mineral matter from the first source can not be removed by washing methods; it is sometimes called the "intrinsic ash" of the coal. Mineral matter from the second source, sometimes called "extraneous ash," may be removed by methods of washing, screening, and picking. In the laboratory a similar separation can be made by the float-and-sink test. Coal has a specific gravity somewhat less than 1.35; the impurities are heavier; hence a separation may be made by placing the coal, crushed to a suitable size, in a solution of calcium or zinc chloride of 1.35 specific gravity. The coal will float, while the shale, bone, pyrites, etc., will sink. In this way the possibility of improving the quality of coal by washing can be determined.

The determination of ash, although one of the simplest operations, is also beset with certain difficulties that lead to disagreement among different laboratories, more especially with coals containing notable quantities of calcium carbonate and iron pyrites. On ignition the calcium carbonate is decomposed, and carbon dioxide driven off, either partially or completely, depending on the duration and temperature of ignition. The iron pyrites is changed to ferric oxide, while more or less of the sulfur combines with the lime to form CaSO₄. For example, in certain experiments with Illinois coals that contained notable quantities of calcium carbonate and sulfur, 14 per cent. ash was obtained by ignition to constant weight at a low-red heat, and 13 per cent. ash was obtained by ignition at a bright-red heat. To secure concordant results a standard temperature should be adopted. If this is done duplicate determinations on the same powdered sample will agree to within 0.2 per cent.

Coal ash as determined usually weighs less than the mineral matter from which it is produced. This is due mainly to the loss of volatile constituents during ignition: the shale and clay will lose their water of composition; the carbonates will be more or less decomposed, giving off carbon dioxide; and the iron pyrites will be changed to ferric oxide, giving off sulfur.

Several methods have been proposed to compute the weight of original mineral matter in the coal, by adding corrections to the weight of ash obtained by ignition. These methods are, however, too complicated and uncertain in their general application to all classes of coal to be used in technical work.

VOLATILE MATTER AND FIXED CARBON

The volatile matter and fixed carbon represent the relative proportions of gaseous and solid combustible matter that may be obtained from the coal by heating it in a closed vessel. This is done by heating a finely powdered sample in a small, covered platinum crucible, in the flame of a Bunsen or Méker

¹ F. M. Stanton and A. C. Fieldner, "Methods of Analyzing Coal and Coke," Bureau of Mines, *Technical Paper 8*.

burner, for exactly seven minutes. The volatile matter consists mainly of the combustible gases—hydrogen, carbon monoxide, methane, and other hydrocarbons—and some non-combustible gases such as carbon dioxide and water vapor. The volatile matter does not include water present in the coal as moisture at 105° C. (221° F.).

The residue of coke left in the crucible after deducting the ash is reported as "fixed carbon." The fixed carbon does not represent the total carbon in the coal, as a portion of this element is driven out in combination with hydrogen in the volatile matter; furthermore, fixed carbon is not pure carbon, but still contains several tenths per cent. each of carbon, hydrogen, and oxygen; from 0.4 to 1.0 per cent. nitrogen; and about half the sulfur that was in the coal. It should be clearly understood that the terms "volatile matter" or "volatile combustible matter" and "fixed carbon" do not represent any definite compounds which existed in the coal before heating. The method of determination is purely arbitrary, and variations in temperature and rate of heating will cause variations amounting to several per cent.; even with a strict adherence to the method recommended by the American Chemical Society, variations of three and four per cent. in both the volatile matter and fixed carbon may occur in different laboratories. One of the most prominent factors in causing variations is the temperature at which the crucible is heated. This is especially pronounced in anthracite and semibituminous coal. It is not improbable for one laboratory to report 4 per cent. and another 7 per cent. volatile matter on the same sample of anthracite, or 14 per cent. and 17 per cent. respectively on the same sample of Pocahontas coal. The different percentages of volatile matter were actually produced by different conditions of heat treatment. Caution must, therefore, be observed in making comparisons of the volatile matter and fixed carbon in proximate analyses made in different laboratories. Even determinations made at the same laboratory by the same analyst may vary to the extent of 0.5 per cent.

Recently a series of experiments was made at the Pittsburgh station of the Bureau of Mines to provide data on which to base a temperature specification at which the most uniform analytical results could be obtained.¹ A series of determinations at temperatures varying from 750° C. (1382° F.) to 1100° C. (2012° F.) were made on five different types of coal and one sample of foundry coke. These determinations were made in a 30 cc. platinum crucible, which was heated in an electric furnace under uniform conditions. Oxidation was prevented by passing nitrogen into the crucible. The results obtained are given in Table I and graphically illustrated in the curves in the accompanying illustration.

It will be seen that more volatile matter is obtained at the higher temperatures, although the ratio between temperature and volatile matter varies in the different coals tested. The curve for anthracite is remarkable

¹ A. C. Fieldner and A. E. Hall, "Influence of Temperature on the Determination of Volatile Matter in Coal," *Eighth International Congress of Applied Chemistry*, 10, 139 (1912).

TABLE I—VOLATILE MATTER AT DIFFERENT TEMPERATURES
Per cent. of volatile matter

C° temper- atures	Coke	Anthracite	Pocahontas	Pittsburgh	Colorado	Illinois
740-745	0.40	32.86	32.99	...
745-750	...	2.84	14.66	32.38
		2.96
750-755	0.51	...	14.80	33.13	33.00	...
755-760	0.56	32.51
765-770	...	2.93
770-775	33.68
785-790	33.69
790-795	33.70	...
795-800	...	3.25	...	33.89
805-810	0.55 } 0.54 }	...	15.85	34.05	34.07	...
810-815	0.60	3.33	...	34.11	...	33.60
815-820	...	3.23
825-830	16.17	33.98
835-840	0.63
840-845	...	3.57
850-855	...	3.59	34.12	...
855-860	0.53	34.70	...	34.54
860-865	0.44	34.75	...	34.63
865-870	...	3.70
870-875	0.53
885-890	16.49
890-895	16.45
895-900	34.99
905-910	34.57
910-915	0.68	3.93 } 4.15 }	34.62	...
915-920	16.70 } 16.92 }	34.75	34.80	...
920-925	35.18
935-940	0.71
955-960	34.93	...
960-965	17.03	35.00	34.94	35.60 } 35.70 }
965-970	0.80	34.92
970-975	0.85	...	17.13
975-980	...	4.63 } 4.63 }
1000-1005	34.87
1005-1010	0.95	...	17.10	34.82	34.97	...
1010-1015	0.91	4.86	35.02	35.55 } 35.86 }
1015-1020	...	5.00
1025-1030	17.30
1050-1055	1.02	35.63
1055-1060	1.02	35.89
1060-1065	34.89	...
1065-1070	...	5.19	17.21 } 17.33 }	34.72 } 34.82 }	34.97	...
1075-1080	...	5.36
1085-1090	17.35
1110-1115	...	5.60	17.49
1120-1125	1.22
1125-1130	...	5.71
1130-1135	1.25

in that it is practically a straight line. The curves for the three bituminous coals become horizontal at about 950° C. (1742° F.). The Pocahontas curve retains a slight upward inclination even at the higher temperatures.

From the analytical standpoint, 950°-1000° C. (1742°-1832° F.) appears to be the best temperature for the determination of volatile matter, as slight variations in temperature on the upper end of the curve produce less deviation in results.

SULFUR

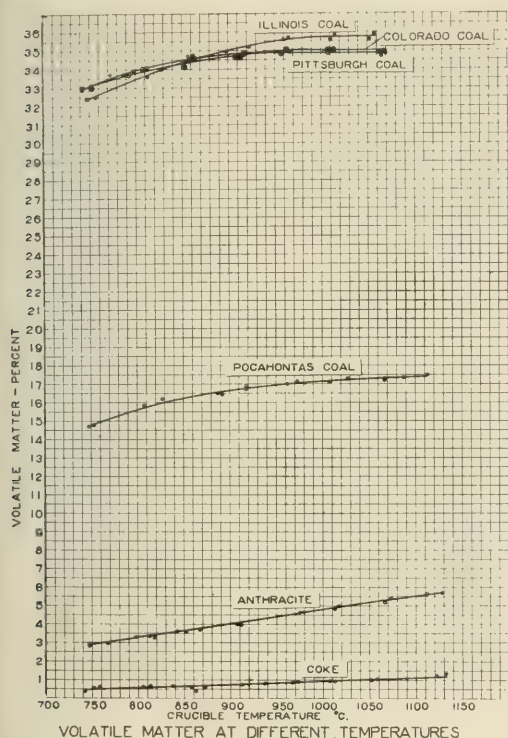
Sulfur is usually determined in connection with the proximate analysis. It is classified with the impurities and undesirable constituents of coal, although it usually exists in a combustible form and contributes to the heating value. Commonly sulfur is present as iron pyrites, either in brassy lumps and bands or

in very fine particles uniformly distributed throughout the coal. Sulfur may also occur in combination with iron and lime as sulfates and in combination with the coal substance as organic compounds.

Duplicate determinations by the "Eschka" method on the same powdered sample will usually agree to within 0.05 per cent. Where much sulfur is present in visible form, as pyrite, difficulty is experienced in obtaining a representative powdered sample from the coarse sample, and somewhat greater errors due to inaccuracies in sampling may occur.

ULTIMATE ANALYSIS

In an ultimate analysis the organic matter of the coal is resolved into its chemical elements, *viz.*, carbon, hydrogen, oxygen, sulfur and nitrogen. These ele-



ments, together with the ash, are taken as equal to 100 per cent. As there is no direct method for the determination of oxygen, it is estimated by subtracting the sum of the other five constituents from 100. This method throws the summation of all the errors incurred in the other determinations upon the oxygen.

The determination of carbon, hydrogen, and nitrogen, while requiring experience and a considerable degree of analytical skill on the part of the chemist, is not subject to the arbitrary conditions that must be maintained in the proximate analysis. As the chemist is dealing with definite chemical elements, he should be able to duplicate his determinations within the following limits: Carbon, 0.3 per cent.; hydrogen, 0.05 per cent.; nitrogen, 0.03 per cent.

It is unfortunate that no direct method has yet

been devised for the determination of oxygen. The percentage of oxygen is an important factor in many of the problems connected with the classification, spontaneous combustion, weathering, and inflammability of coal. In the present method of estimation the oxygen percentage is subject to an error equal to the algebraic sum of the individual errors incurred in the determinations of carbon, hydrogen, nitrogen, sulfur, and ash. The most serious of these errors is due to the difference in weight between the ash and the mineral matter (exclusive of sulfur, which is separately determined) as it occurs in the coal. For instance, if all the sulfur is present as iron pyrites, the oxygen percentage will have a negative error equal to three-eighths of the sulfur. This correction, however, is applicable only when the percentage of pyritic sulfur is known, and a satisfactory method for determining all the different forms of sulfur found in coal is yet to be devised. Furthermore, there are errors in the opposite direction that tend to compensate the error due to the oxidation of iron pyrites, notably the loss of certain mineral constituents like carbon dioxide from carbonates and water of composition from the shaly constituents.¹ Prof. Parr has found the water of composition in Illinois coals to be approximately 8 per cent. of the ash. In a coal with 10 per cent. ash this would cause an error of +0.71 per cent. in the oxygen; if this same coal happened to contain 2 per cent. sulfur as iron pyrite, an additional error of -0.75 per cent. would be incurred in the oxygen. The two errors would thus compensate to within 0.04 per cent.; whether the final oxygen error is positive or negative would depend upon the relative proportions of shale and pyrite in the coal, and upon the quantities of carbonates of iron and lime. It is doubtful if any generally applied method of correction would materially increase the accuracy of the oxygen result.

The ultimate analysis as usually made does not distinguish between the carbon and hydrogen derived from the organic or combustible matter of the coal, and the small proportion of these elements that may be present in an incombustible form in the mineral impurities. Illinois coals, as shown by Prof. Parr² often contain 0.1-0.7 per cent. carbon as calcium carbonate. Most of the coal in the Appalachian field is comparatively free from carbonates. A small proportion of the hydrogen, usually from a few hundredths to about 0.1 per cent., has its origin in the water of composition of the clay or shaly material. While corrections can be made with the aid of special chemical methods for the small percentages of inorganic carbon, hydrogen, and oxygen, it is not necessary in the ordinary technical analyses.

In the consideration of an ultimate analysis it must be kept in mind that the hydrogen and oxygen of the moisture in the sample are included with the hydrogen and oxygen of the dry coal substance. Usually before making comparisons, ultimate analyses are computed to a dry-coal basis, thus giving the relative propor-

¹ S. W. Parr, Ill. State Geol. Survey, *Bull.* 8, 154.

² Ill. State Geol. Survey, *Bull.* 16, 232.

tions of hydrogen and oxygen in the dry coal.

The term "available hydrogen," often used in the computation of the calorific value of a coal from the ultimate analysis, is based on the assumption that all the oxygen in the coal is combined with hydrogen in the proper ratio to form water. The amount of hydrogen thus combined and not available for producing heat is equal to one-eighth of the oxygen; the remainder of the hydrogen, or "available hydrogen," is combined with the carbon and contributes to the heating value of the coal. This hypothesis is fairly well supported in the case of anthracite and bituminous coals by the general agreement of calorific values calculated from the ultimate analysis by Dulong's formula with the values determined by the bomb calorimeter.

CALORIFIC VALUE

The calorific value of a fuel is the total quantity of heat developed by the complete combustion of the unit weight of fuel. In the metric system of measurement which is usually used by chemists and physicists, the heat units are the gram calorie and the kilogram calorie. The gram calorie, or small calorie (cal.), is the amount of heat required to raise the temperature of one gram of water 1° C. at 15° C. and the kilogram calorie, or large calorie (Cal.), is the amount of heat required to raise the temperature of one kilogram of water 1° at 15° C.

In the English system which is generally used by engineers, the heat unit is the "British Thermal Unit," or B. t. u. The British thermal unit is the quantity of heat required to raise the temperature of one pound of water, 1° F., at 60° F. Calorific values given in calories per gram may be converted into British thermal units per pound, by multiplying by 1.8, because the temperature rise produced in one gram of water by the heat in one gram of coal will be the same as the rise produced in one pound of water by the heat in one pound of coal, hence, the relation between the calorific values of one gram and one pound of fuel is simply that of the two different thermometric scales, which is 9/5.

The most accurate method of determining the total heating value is by combustion in a bomb calorimeter. The instrument should be carefully standardized by burning substances of known calorific value such as the standard samples of cane sugar, naphthalene, and benzoic acid, that are now being furnished by the Bureau of Standards. The standardization should be conducted under exactly the same conditions, and with the same thermometer that is used in the tests. The use of calibrated thermometers is essential. In carefully conducted calorimetric work the probable error should not exceed 0.3 per cent., which corresponds to about 50 B. t. u. in a high-grade coal. This is a higher degree of accuracy than can be obtained in the usual methods of sampling, which oftentimes increase the error to 100 B. t. u.

CALCULATION OF CALORIFIC VALUE BY DULONG'S FORMULA

Before the bomb calorimeter came into general

use, the heating value of a coal was frequently calculated from the ultimate analysis by Dulong's formula:

$$(1) \text{ Calorific value in calories per gram} = 8080 C + 34460 (H - 0/8) + 2250 S.$$

$$(2) \text{ Calorific value in B. t. u. per pound} = 14544 C + 62028 (H - 0/8) + 4050 S.$$

In the above formulas, C, H, O, and S are the respective proportions of carbon, hydrogen, oxygen and sulfur.

Aside from the fact that an ultimate analysis is more expensive and time-consuming than a calorimetric determination, there are the following theoretical objections to be considered:

(1) The heating value of the elements—carbon, hydrogen, and sulfur, as given in the formula—have not been established with any great degree of accuracy.

(2) The heating value of an element in the free state and as a component of a chemical compound is not necessarily the same; as a matter of fact it usually varies, due to absorption or evolution of heat in forming the compound.

(3) The usual assumption that from the standpoint of heat development all the oxygen is combined with hydrogen, may not be true; some of the oxygen may be linked with carbon.

(4) The relative accuracy of the calculated results are subject to the uncertainty of the oxygen estimation.

On the other hand, in spite of the objections just cited, there is fairly close agreement between the calorific values calculated by Dulong's formula and those determined by the calorimeter. Lord and Somermeier,¹ in a large series of analyses of the coals of Ohio, found that with very few exceptions the results obtained by Dulong's formula were within 1—1½ per cent. of the values obtained with the bomb calorimeter. This degree of accuracy has also been found to hold true with anthracite, semi-bituminous and bituminous coals of various parts of the United States as shown in Table II.

TABLE II—A COMPARISON OF CALORIFIC VALUES AS DETERMINED IN THE BOMB CALORIMETER AND AS CALCULATED FROM THE ULTIMATE ANALYSIS BY DULONG'S FORMULA

Calorific value in B. t. u. per pound = 14544 C + 62028 (H—0/8) + 4050S									
Description	Lab. no.	Proximate analysis, dry basis			Calorific value, dry basis			Error in calculated calorific value	
		Moisture per cent.	Ash per cent.	Vol. matter per cent.	Deter. B. t. u.	Calcu. B. t. u.	Difference B. t. u.	Per cent.	Per cent.
Dry peat									
Mass.....	12767	...	20.1	56.3	7745	7452	—293	—3.8	
Mass.....	12766	...	11.2	64.2	9018	8477	—541	—6.0	
Mass.....	10834	...	4.0	65.6	10285	9629	—656	—6.4	
Mass.....	10833	...	4.0	64.4	10305	9718	—587	—5.7	
Maine.....	5978	...	5.2	70.0	8471	7542	—929	—11.0	
Maine.....	5983	...	3.8	67.6	9598	8600	—998	—10.4	
Maine.....	5994	...	6.7	70.3	8132	7319	—813	—10.0	
Maine.....	5975	...	3.8	66.6	8915	7974	—941	—10.6	
Mich.....	6270	...	14.4	57.5	9139	8423	—716	—7.9	
Wisc.....	6880	...	17.3	58.0	8149	7489	—660	—8.1	
Wisc.....	6507	...	18.7	55.8	7835	7606	—229	—2.9	
Wisc.....	6290	...	26.2	59.2	7465	7002	—463	—6.2	
Mean algebraic error in 12 samples.....									—7.4
Maximum error.....									—11.0

¹ Geological Survey of Ohio, 4th series, *Bull.* 9, 267 (1908).

TABLE II (Continued)

Description	Lab. no	Proximate analysis as received			Calorific value as received			Error in calculated calorific value Per cent.
		Mois- ture Per cent.	Ash matter Per cent.	Volatiles Per cent.	Deter- mined B. t. u.	Calcu- lated B. t. u.	Dif- ference B. t. u.	
Lignite								
Valley Co.								
Mont.....	10898	42.8	4.6	25.7	6105	5785	-320	-5.2
Mont.....	10899	41.3	4.8	25.7	6260	5974	-286	-4.6
Mont.....	10900	41.6	4.1	27.1	5733	5467	-266	-4.7
Mont.....	10725	38.9	6.2	27.2	6014	5843	-171	-2.8
Mont.....	10726	35.3	7.7	31.8	5404	5227	-177	-3.3
Mont.....	10727	37.5	6.1	26.8	6580	6408	-172	-2.6
Mont.....	10724	32.6	9.1	27.4	6712	6664	-48	-0.7
Mont.....	11002	40.4	7.5	24.5	5830	5598	-232	-4.0
Mont.....	11003	39.3	5.7	24.2	6278	6059	-219	-3.5
Mont.....	11004	37.7	5.5	25.8	6700	6550	-150	-2.3
Mont.....	11005	40.7	6.2	25.2	6147	5980	-167	-2.7
Mont.....	11006	41.6	5.6	26.7	5278	4991	-287	-5.4
Morton Co.								
N. D.....	14729	36.2	8.7	29.8	6700	6559	-141	-2.1
N. D.....	1416	36.8	5.1	28.2	7204	6928	-276	-3.9
Perkins Co.								
S. D.....	12488	42.5	9.0	23.2	5954	5913	-41	-0.7
S. D.....	12453	39.2	8.4	24.7	6307	6277	-30	-0.5
Texas.....	1456	34.7	11.2	32.2	7056	6849	-207	-2.9
Texas.....	1597	33.7	7.3	24.3	7348	7155	-193	-2.6
Texas.....	2717	33.9	7.3	27.5	7497	7204	-293	-3.9
Mean algebraic error in 19 samples.....								-3.1
Maximum error in 19 samples.....								-5.4
Sub-bituminous coal, Rocky Mountain field								
Colorado								
El Paso Co...	10732	31.1	13.9	26.0	6199	6237	38	0.6
El Paso Co...	12099	26.2	6.5	29.7	8352	8114	-238	-2.8
El Paso Co...	10741	33.7	18.2	23.5	5506	5542	36	0.7
Wyoming								
Converse Co.	11048	28.1	4.6	31.6	8350	8057	-293	-3.5
Converse Co.	10775	27.7	10.0	26.7	7808	7763	-45	-0.6
Converse Co.	10740	27.9	8.3	27.1	7927	8001	74	0.9
Fremont Co.	10843	20.9	3.7	32.0	9781	9673	-108	-1.1
Fremont Co.	10842	21.1	5.8	31.4	9463	9293	-170	-1.8
Johnson Co.	11059	16.8	15.0	31.4	8480	8440	-40	-0.5
Johnson Co.	10827	23.5	5.2	35.6	9050	8719	-331	-3.8
Sheridan Co.	10810	22.7	3.4	32.2	9344	9221	-123	-1.3
Sheridan Co.	10811	24.7	3.7	31.8	9007	8852	-155	-1.7
Sheridan Co.	10825	22.6	4.6	32.5	9218	9131	-87	-1.0
Sheridan Co.	10826	22.1	4.4	33.4	9256	9378	122	1.3
Sheridan Co.	10822	23.5	4.9	31.2	9121	8935	-186	-2.0
Sheridan Co.	12005	22.3	3.7	35.0	9617	9364	-253	-2.6
Sheridan Co.	12008	23.1	3.2	31.9	9484	9302	-182	-1.9
Sheridan Co.	12006	23.4	3.6	33.6	9392	9259	-133	-1.4
Sweetwater Co.	11510	16.3	2.1	34.9	11153	11086	-67	-0.6
Sweetwater Co.	11460	13.1	3.4	35.8	11619	11576	-43	-0.4
Mean algebraic error in 20 samples.....								-1.4
Maximum negative error.....								3.8
Maximum positive error.....								0.9

Bituminous coal
Rocky Mt. field
Canada

Alberta.....	14883	10.6	16.7	36.4	9819	9828	9	0.1
Alberta.....	14882	9.8	6.8	40.2	11412	11385	-27	-0.2
Alberta.....	13177	6.5	16.2	34.5	10737	10582	-155	-1.4
Alberta.....	12737	2.0	17.6	27.4	12208	12166	-42	-0.4
Colorado								
La Plata Co.....	14775	7.1	5.9	38.1	12672	12649	-23	-0.2
La Plata Co.....	14772	3.0	6.9	34.8	13714	13853	139	1.0
Fremont Co.....	13395	10.3	5.5	38.3	11416	11230	-186	-1.6
Las Animas Co.13364	3.3	15.6	32.0	12357	12175	-182	-1.4	
Las Animas Co.13254	5.4	8.6	33.0	13237	13176	-61	-0.5	
Las Animas Co.13253	6.3	14.1	30.2	12145	12121	-24	-0.2	

New Mexico

Colfax Co.....	13367	5.6	13.2	35.8	12019	12015	-4	■
Colfax Co.....	12235	3.3	12.3	35.7	12757	12773	16	0.1
Colfax Co.....	12338	3.6	12.0	36.1	12623	12580	-43	-0.3

Utah

Carbon Co.....	10906	7.5	5.6	39.7	12521	12523	2	0
Carbon Co.....	10909	5.7	7.0	40.8	12647	12605	-42	-0.3
Oregon.....	12825	3.3	7.2	40.3	12640	12597	-43	-0.3

TABLE II—Continued

Description	Lab. no.	Proximate analysis as received			Calorific value as received			Error in calculated calorific value Per cent.
		Mois- ture Per cent.	Ash matter Per cent.	Volatiles Per cent.	Deter- mined B. t. u.	Calcu- lated B. t. u.	Dif- ference B. t. u.	
Oregon.....	12824	2.5	8.6	37.3	13039	13070	-31	-0.2
Washington								
Kittitas Co.....	11525	3.9	12.6	37.0	12434	12546	112	0.9
Kittitas Co.....	11526	3.8	11.5	37.7	12762	12840	78	0.6
Wyoming								
Uinta Co.....	11565	5.7	5.3	37.7	12580	12451	-129	-1.0
Mean algebraic error in 20 samples.....								-0.3
Maximum negative error.....								1.6
Maximum positive error.....								1.0
Bituminous coal								
Illinois field								
Grundy Co.								
Bed No. 2.....	14926	6.9	6.0	40.0	12290	12206	-84	-0.7
La Salle Co.								
Bed No. 2.....	14923	5.1	9.7	41.9	12092	12139	47	0.4
Bed No. 2.....	14922	6.8	9.5	41.0	11808	11732	-76	-0.6
Bureau Co.								
Bed No. 2.....	14921	5.2	9.5	40.1	12078	11974	-104	-0.9
Clinton Co.								
Bed No. 6.....	14712	8.4	10.3	37.5	11313	11302	-11	-0.1
Bed No. 6.....	14711	7.8	10.7	38.5	11324	11363	39	0.3
Randolph Co.								
Bed No. 6.....	14710	5.8	12.1	38.9	11399	11376	-23	-0.2
St. Clair Co.								
Bed No. 6.....	14709	5.3	11.6	41.1	11700	11531	-169	-1.4
Bed No. 6.....	14708	6.6	10.6	41.4	11637	11529	-108	-0.9
Bed No. 6.....	14706	4.5	10.7	42.3	11923	11878	-45	-0.4
Montgomery Co.								
Bed No. 6.....	14704	6.2	11.7	39.9	11534	11493	-41	-0.4
Sangamon Co.								
Bed No. 6.....	14703	5.9	10.2	40.7	11691	11905	214	1.7
Bed No. 6.....	14702	8.4	10.8	39.6	11122	11137	15	0.1
Bed No. 6.....	14701	7.9	9.1	40.7	11527	11515	-12	-0.1
Madison Co.								
Bed No. 6.....	14700	9.0	10.5	40.2	11164	11084	-80	-0.7
Bed No. 6.....	14699	8.0	11.0	40.2	11322	11201	-121	-1.0
Williamson Co.								
Bed No. 6.....	14697	5.3	8.7	37.3	12299	12164	-135	-1.1
Bed No. 6.....	14696	6.8	8.1	33.9	12159	12049	-110	-0.9
Bed No. 6.....	14695	6.8	7.4	34.9	12258	12094	-164	-1.3
Bed No. 6.....	14694	7.2	9.5	33.0	11902	11893	-9	0.1
Franklin Co.								
Bed No. 6.....	14692	5.3	10.8	35.4	11974	12163	189	1.5
Bed No. 6.....	14691	6.4	7.9	34.5	12253	12256	3	0
Bed No. 6.....	14690	4.6	13.2	40.0	11749	11936	187	1.6
Fulton Co.								
Bed No. 5.....	14688	4.5	12.9	39.1	11633	11821	188	1.6
Bed No. 5.....	14687	5.7	12.0	38.7	11500	11657	157	1.4
Mean algebraic error in 30 samples.....								-0.1
Maximum negative error.....								1.4
Maximum positive error.....								1.7

Bituminous coal
Appalachian field
Pennsylvania
Allegheny Co.

Pgh. bed.....	14879	3.3	6.4	36.2	13619	13799	180	1.3
Pgh. bed.....	14855	2.7	5.6	37.2	13820	13829	9	0.1
Pgh. bed.....	14849	1.9	5.1	37.0	14008	14159	151	1.1
Pgh. bed.....	13389	2.4	4.7	36.7	14058	13999	-59	-0.4
Pgh. bed.....	12579	2.7	14.9	34.9	12325	12323	-2	0
Pgh. bed.....	12578	3.4	5.3	35.9	13734	13777	43	0.3
Pgh. bed.....	12577	3.2	8.5	34.6	13279	13322	43	0.3
Pgh. bed.....	12576	2.9	5.6	37.0	13817	13921	104	0.8
Pgh. bed.....	12574	3.0	5.4	37.7	13806	13925	119	0.8
Pgh. bed.....	12573	3.1	5.8	36.8	13738	13705	-33	-0.3
Pgh. bed.....	12572	2.9	5.7	36.2	13761	13889	128	0.9
Westmoreland Co.								
Pgh. bed.....	12853	2.5	10.4	30.3	13365	13450	85	0.6
West Virginia								
Marshall Co.								
Pgh. bed.....	14488	3.4	7.0	41.6	13313	13279	-34	-0.3
Kentucky								
Bed No. 9.....	13260	3.1	7.6	37.8	12208	12191	-17	-0.1

TABLE II—(Continued)

Description	Lab. no.	Proximate analysis as received			Calorific value as received		Error in calculated calorific value	
		Mois- ture Per cent.	Ash Per cent.	Volatile matter Per cent.	Deter- mined B. t. u.	Calcu- lated B. t. u.	Dif- ference B. t. u.	Per cent.
Tennessee								
Anderson Co. 13290	1.9	8.6	35.0	13777	13862	85	0.6	
Anderson Co. 13265	1.5	9.2	35.9	13615	13534	-81	-0.6	
Anderson Co. 13264	1.7	10.1	35.0	13462	13559	97	0.7	
Anderson Co. 13238	1.9	11.5	33.0	13151	13250	99	0.7	
Anderson Co. 13237	1.6	6.6	35.4	14047	14011	-36	-0.3	
Alabama								
Shelby Co.... 13466	3.9	7.5	35.1	13343	13370	27	0.2	
Shelby Co.... 13465	5.8	6.5	34.0	13298	13408	110	0.8	
Shelby Co.... 13464	2.6	4.9	35.4	14202	14067	-135	-0.9	
Shelby Co.... 13463	2.1	4.0	36.5	14447	14225	-222	-1.5	
Walker Co.... 13462	3.8	9.4	37.7	12895	12841	-54	-0.4	
Walker Co.... 13461	3.0	9.1	39.7	13118	13279	161	1.2	
Walker Co.... 13460	4.6	13.2	35.9	12056	12204	148	1.2	
Walker Co.... 13459	3.7	9.3	37.9	12992	12946	-46	-0.4	
Walker Co.... 13187	1.1	16.1	26.4	12793	12825	32	0.2	
Walker Co.... 13186	1.0	4.9	29.8	14647	14742	95	0.7	
Walker Co.... 13185	2.0	5.0	35.5	13997	13968	-19	-0.1	
Mean algebraic error in 30 samples.....								0.2
Maximum negative error in 30 samples.....								1.5
Maximum positive error in 30 samples.....								1.3

Semi-bituminous coal, Appalachian field

Pennsylvania								
Cambria Co.								
"B" bed..... 14243	2.7	4.6	18.1	14560	14645	85	0.6	
"B" bed..... 12377	0.8	6.7	20.4	14549	14537	-12	-0.1	
"B" bed..... 12376	0.8	9.4	21.4	14022	14207	185	1.3	
"B" bed..... 12375	0.8	6.3	20.8	14531	14683	152	1.0	
"B" bed..... 12374	0.8	6.1	20.0	14605	14688	83	0.6	
Indiana Co.								
"E" bed..... 12373	1.0	9.1	26.1	13945	14038	93	0.7	
Cambria Co.								
"B" bed..... 12372	0.8	7.2	22.9	14443	14575	132	0.9	
"B" bed..... 12371	0.8	9.1	23.9	14040	14116	76	0.5	
"B" bed..... 12370	0.9	6.7	23.1	14485	14575	90	0.6	
"C" bed..... 12369	0.9	8.9	18.4	14081	14157	76	0.5	
Clearfield Co.								
"B" bed..... 12368	0.8	10.9	20.4	13734	13876	42	0.3	
"B" bed..... 12367	0.9	9.0	21.6	14060	14198	138	1.0	
West Virginia								
McDowell Co.								
Pocahontas bed 14424	2.0	6.8	17.8	14324	14504	180	1.3	
Pocahontas bed 14420	1.6	5.9	18.0	14508	14598	90	0.6	
Pocahontas bed 14399	2.8	4.6	17.7	14573	14663	90	0.6	
Pocahontas bed 14282	4.2	3.2	18.6	14629	14551	-78	-0.5	
Pocahontas bed 14276	3.8	3.2	18.3	14690	14791	101	0.7	
Mercer Co.								
Pocahontas..... 14260	3.1	3.9	18.2	14688	14823	135	0.9	
Pocahontas..... 14237	3.2	3.7	17.0	14729	14848	119	0.1	
McDowell Co.								
Beckley bed.... 14472	2.2	8.9	17.3	13952	14058	106	0.8	
Beckley bed.... 14430	2.6	8.2	17.2	14006	14137	131	0.9	
Beckley bed.... 14408	2.2	8.4	16.4	14006	14017	11	0.1	
Beckley bed.... 14269	2.3	11.1	16.8	13514	13727	213	1.6	
Raleigh Co.								
Beckley bed.... 14291	3.3	4.3	19.0	14519	14627	108	0.7	
Beckley bed.... 14309	2.2	3.5	17.2	14738	14855	117	0.8	
Beckley bed.... 14317	3.3	3.3	17.4	14704	14839	135	0.9	
Beckley bed.... 14318	3.7	2.9	17.2	14668	14816	148	1.0	
Fayette Co.								
Sewell bed..... 14404	3.0	3.1	25.7	14605	14717	112	0.8	
Sewell bed..... 14362	3.0	3.8	28.0	14423	14512	89	0.6	
Sewell bed..... 14345	2.9	2.3	25.6	14796	14854	58	0.4	
Mean algebraic error in 30 samples.....								0.7
Maximum negative error in 30 samples.....								1.6
Maximum positive error in 30 samples.....								0.5

Anthracite

Pennsylvania... 14765	4.0	12.2	8.9	12591	12555	-36	-0.3	
Pennsylvania... 14764	3.9	14.7	8.5	12179	12231	52	0.4	
Pennsylvania... 14763	4.9	15.4	9.5	11954	12047	93	0.8	
Pennsylvania... 14762	3.2	16.4	8.0	11939	12020	81	0.7	
Pennsylvania... 14761	3.2	11.5	9.3	12971	13043	72	0.6	

TABLE II—(Continued)

Description	Lab. no.	Proximate analysis as received			Calorific value as received		Error in calculated calorific value	
		Mois- ture Per cent.	Ash Per cent.	Volatile matter Per cent.	Deter- mined B. t. u.	Calcu- lated B. t. u.	Dif- ference B. t. u.	Per cent.
Pennsylvania... 14760	1.6	19.7	12.2	11929	12001	72	0.6	
Pennsylvania... 14759	0.9	18.8	12.1	12227	12416	189	1.5	
Pennsylvania... 14758	3.8	18.4	7.1	12333	11392	59	0.5	
Pennsylvania... 14757	1.7	17.6	10.7	12136	12238	102	0.8	
Pennsylvania... 14720	2.0	17.9	8.1	11875	11920	47	0.4	
Pennsylvania... 14719	2.7	19.7	8.4	11578	11662	84	0.7	
Pennsylvania... 14718	3.1	16.2	8.9	11916	11990	74	0.6	
Pennsylvania... 14520	3.0	15.1	6.4	12038	12125	87	0.7	
Pennsylvania... 14209	3.8	17.1	8.2	11781	11777	-4	0	
Pennsylvania... 14208	3.6	14.4	7.2	12137	12222	85	0.7	
Pennsylvania								
Sullivan Co... 9664	3.6	11.9	9.1	13072	13212	140	1.1	
Sullivan Co... 9665	3.4	11.5	8.5	13156	13273	117	0.9	
Sullivan Co... 9652	3.4	11.7	9.3	13120	13221	101	0.8	
Sullivan Co... 9653	3.7	13.1	9.2	12836	12870	34	0.3	
Sullivan Co... 9654	3.4	15.6	8.4	12497	12569	72	0.6	
Mean algebraic error in 20 samples.....								0.6
Maximum negative error in 20 samples.....								0.3
Maximum positive error in 20 samples.....								1.5

A total of 176 analyses were selected at random from the records of the chemical laboratory without any attempt whatever towards selecting concordant or diverging results, but simply taking them from the laboratory record as they happened to occur. Enough analyses were selected to secure about 20 to 30 samples of each representative class of coal from the most recent lignites, through the range of sub-bituminous, bituminous, semi-bituminous and anthracite coals of Pennsylvania. For comparison a number of peats are also included.

The tabulation brings out in a striking manner the variation in the relation between the heating value calculated by Dulong's formula and the true heating value as determined in the bomb calorimeter. This relation is within certain limits, characteristic of the class of coal. For instance, in coals low in volatile matter and oxygen, like anthracite and Pocahontas coal, the calculated value is usually from 0.3 to 1.5 per cent. greater than the determined value. In only very few instances is the calculated value less than the determined value; in the bituminous coals the calculated values vary both above and below the determined values usually within limits of 1.5 per cent.; in sub-

TABLE III—A SUMMARY OF THE MEAN ALGEBRAIC, MAXIMUM POSITIVE, AND MAXIMUM NEGATIVE ERRORS, IN THE CALORIFIC VALUES CALCULATED BY DULONG'S FORMULA, AS FOUND IN GROUPS OF 20 TO 30 REPRESENTATIVE ANALYSES OF EACH CLASS OF COAL

Class of coal	Error in calculated calorific value			Oxygen in coal, Moisture-and-ash-free
	Mean algebraic error	Maximum plus error	Maximum minus error	
	Per cent.	Per cent.	Per cent.	Per cent.
Peat.....	-7.4	...	11.0	34.4
Lignite, Dakotas, Mont. & Texas..	-3.1	...	5.4	23.4
Sub-bituminous, Rocky Mt. field..	-1.4	0.9	3.8	19.1
Bituminous, Rocky Mt. field.....	-0.3	1.0	1.6	9.8
Bituminous, Illinois field.....	-0.1	1.7	1.4	10.7
Bituminous, Appalachian field....	+0.2	1.3	1.5	7.1
Semi-bituminous, Pa. and W. Va..	+0.7	1.6	0.5	3.1
Anthracite, Pennsylvania.....	+0.6	1.5	0.3	3.1

bituminous and lignitic coals the calculated value becomes less and less than the determined value as

the oxygen increases, the deviation often reaching 4 and 5 per cent.; in peat the calculated results are quite unreliable, the results being from 3 to 11 per cent. low.

A summary of Table II, giving the maximum, minimum and mean error in the calculated values, together with the average moisture-and-ash-free oxygen for each class of coal, is given in Table III.

The progressive change in the Dulong values, with the increase in oxygen, is significant and points to a combination of part of the oxygen with carbon in highly oxygenated coals. Porter and Ovitz¹ have already arrived at this conclusion from a consideration of data obtained in their studies of the volatile matter obtained by destructive distillation.

CALCULATION OF CALORIFIC VALUE FROM THE PROXIMATE ANALYSES

The calculation of calorific values by formulae depending on the proximate analysis is apt to give quite erroneous results. Such methods are subject to the considerable uncertainty of the fixed carbon and volatile matter determinations. Furthermore, the variable proportion of inert volatile matter, which does not contribute to the heating value, is not taken into consideration.

Use of "Moisture-and-Ash-Free" Values.—A fairly accurate and simple method of calculating the heating value of Appalachian, bituminous, and semi-bituminous coal from the same mine and seam is based on the constancy in heating value of the "combustible" or coal substance free of moisture and ash.

The calorific value of a coal may be referred to a moisture-and-ash-free basis by dividing the calorific value as determined by one minus the sum of the moisture and ash in the unit weight of fuel.

Moisture-and-ash-free calorific value

$$= \frac{\text{Calorific value as determined}}{1 - (\text{moisture} + \text{ash})}$$

This so-called moisture-and-ash-free calorific value, which represents approximately the heating power of the combustible in the coal, has been found fairly constant for the same coal bed over limited areas, such as are covered by several adjacent mines.

TABLE IV—VARIATIONS IN "MOISTURE-AND-ASH-FREE" CALORIFIC VALUES OF MINE SAMPLES FROM THE SAME MINE

Locality and coal bed	"Moisture-and-ash-free" calorific values of individual samples B. t. u.	Average B. t. u.	Maximum difference of individual samples		Maximum deviation from average	
			Per B. t. u. cent.	Per B. t. u. cent.	Per B. t. u. cent.	Per B. t. u. cent.
5 samples from a mine near Figert, Pa., in Cambria Co., Middle Kittanning bed.....	15600 15600 15640 15610 15650	15620	50	0.3	30	0.2
5 samples from a mine near Barnesboro, Pa., in Cambria Co., Lower Kittanning or "B" bed	15710 15670 15830 15760 15660	15726	170	1.1	104	0.7
5 samples from a mine near Carrollton, Pa., in Cambria Co., Lower Kittanning or "B" bed	15670 15660 15740 15670 15820	15712	160	1.1	108	0.7
27 samples from mines near Twin Rocks, Pa., in Cambria Co., Lower Kittanning or "B" bed	15820 15730 15890 15780 15730 15710 15770 15820 15700 15800 15690 15700 15740 15770 15840 15720 15760 15740 15740 15760 15790 15770 15840 15750 15780 15830 15820	15770	200	1.3	120	0.8
10 samples from two adjacent mines near Clymer, Pa., in Indiana Co., Lower Kittanning or "B" bed ..	15680 15700 15750 15610 15710 15740 15740 15650 15710 15700	15700	140	0.9	90	0.6
5 samples from a mine near Beaverdale, Pa., Cambria Co., Lower Kittanning or "B" bed	15741 15768 15721 15772 15759	15752	51	0.3	31	0.2
5 samples from a mine near El Moro, Pa., in Cambria Co., Lower Kittanning or "B" bed	15763 15862 15611 15772 15887	15779	276	1.8	169	1.1
4 samples from a mine near Masontown, Preston Co., W. Va., Upper Freeport bed	15490 15470 15380 15460	15450	110	0.8	70	0.5
5 samples from a mine near Richard, Monongalia Co., W. Va., Upper Freeport bed	15530 15500 15470 15400 15510	15482	130	0.9	82	0.4
6 samples from a mine near Barnesboro, Pa., Cambria Co., Lower Freeport bed	15600 15570 15600 15660 15640 15650	15620	90	0.6	40	0.3
9 samples from a mine near Spangler, Pa., Cambria Co., Lower Freeport bed	15671 15651 15644 15656 15727 15678 15623 15705 15700	15662	204	1.3	139	0.9
10 samples from a mine near Hastings, Pa., Cambria Co., Lower Freeport bed	15698 15678 15646 15588 15604 15590 15655 15638 15608 15647	15635	110	0.8	63	0.4
4 samples from a mine near Dante, Russell Co., Va., Upper Banner bed.....	15426 15521 15408 15476	15458	113	0.8	63	0.4

¹ H. C. Porter and F. K. Ovitz, "The Volatile Matter of Coal," Bureau of Mines, Bull. 1, 1910.

TABLE IV—(Continued)

Locality and coal bed	"Moisture and ash-free" calorific values of individual samples B. t. u.	Average B. t. u.	Maximum difference of individual samples		Maximum deviation from average	
			Per B. t. u. cent.		Per B. t. u. cent.	
23 samples from the government experimental mine near Bruceton, Pa., Allegheny Co., Pittsburgh bed	15140 15190 15170 15110 15160 14960 14930 15030 15070 15080 15040 15040 15070 15140 15070 15080 15140 15140 15140 15100 15060 15050 15080	15087	260	1.7	157	1.0
Car samples from 27 cars of coal delivered to testing station from Dec., 1910, to May, 1911, from a mine near Meadowlands, Washington Co., Pa., Pittsburg bed	14800 14910 14890 15040 14760 14950 14880 14880 14840 14900 14870 14860 14800 14830 14920 14800 14900 14810 14990 14840 14880 14880 14910 14850 14950 14840 14900	14874	280	2.0	166	1.1
Car samples from 4 cars of coal delivered to testing station from Dec. 19, 1910, to Jan., 1911, from another mine near Meadowlands, Washington Co., Pa., Pittsburgh bed	14560 14640 14640 14630	14618	80	0.6	58	0.4
Car samples from 7 cars of coal delivered to testing station from May, 1911, to July, 1911, from a mine near Burgettstown, Washington Co., Pa., Pittsburgh bed	14750 14680 14690 14790 14650 14750 14890	14743	240	1.6	147	1.0
Car samples from 44 cars of coal delivered to testing station from Aug., 1911, to April, 1912, from a mine near Arnold, Westmoreland Co., Pa., Upper Freeport bed	15180 15250 15180 15200 15190 15260 15240 15280 15190 14250 15300 15220 15170 15210 15290 15210 15220 15220 15180 15240 15100 15180 15220 15250 15190 15180 15220 15190 15220 15210 15300 15250 15290 15250 15280 15300 15100 15270 15230 15250 15230 15280 15250 15220	15226	200	1.3	126	0.8
Car samples from 5 cars of coal delivered to testing station from Nov., 1911, to June, 1912, from a mine near Monongahela City, Westmoreland Co., Pa., Pittsburgh bed	15280 15140 15150 15210 15150	15186	140	0.9	94	0.6
Car samples from 3 cars of coal delivered to testing station from Nov., 1911, to May, 1912, from a mine near Greensburg, Westmoreland Co., Pa., Pittsburgh bed	15350 15310 15400	15353	90	0.6	47	0.3

In Table IV are given some "moisture-and-ash-free" calorific values of mine samples taken by engineers of the bureau at different points in a number of mines in Pennsylvania. They are typical in showing the usual range of variation that is found in samples from different parts of a mine.

In the latter part of Table IV is given some data on the variation in "moisture-and-ash-free" calorific values that have been found in car samples of coal delivered to the power plant of the Pittsburgh Experiment Station for fuel purposes. While each set of cars grouped together is supposed to have come from the same mine, they were not loaded under the inspection of a representative of the bureau; also, the coal may have had more or less opportunity for weathering in transit to the testing station. This would explain the slightly larger variations in the car samples.

The greatest deviation in "moisture-and-ash-free" calorific value of any one individual sample from the average of the mine is usually less than one per cent. In only two cases does it reach the maximum figure of 1.1 per cent. Obviously the calorific value of samples representing various shipments of coal from the same mine and seam can be calculated with an accuracy of about 1 per cent. by multiplying the average "moisture-and-ash-free" calorific value of the coal by 1 minus the sum of the moisture and ash of the various individual samples. This method of calculating will not apply to weathered coals which on account of absorption of oxygen have lost some of their original heating value, or to coals that vary considerably in the character and amount of ash and sulfur. In the coals cited in Table IV the ash is usually less than 12 per cent. and the sulfur less than 2.0 per cent.

Where the sulfur content is larger and more variable, as in some of the coals of Ohio¹ and Illinois,² a further correction for the influence of sulfur should be applied.

SAMPLING

The chemist makes his analysis on a few ounces of powdered coal. If the analysis is to be of any value, this small sample must have a composition that is an average of the entire lot of coal whose value is to be established. Non-representative samples are misleading and frequently lead to much controversy as well as financial loss. Therefore, sampling should never be placed in inexperienced hands. It is just as important for the chemist to devise and direct the method of taking samples as it is for him to make the analyses. The sampling of shipments and deliveries of coal involves special difficulties on account of the usual admixture of pieces of slate, bone and other impurities, with the lumps of coal. The mechanical methods which have been found satisfactory in sampling ore can not be used for the ordinary sizes of coal on account of destroying the value of the fuel by the necessary crushing. The accuracy of sampling the commercial sizes of coal is limited to the amount

¹ N. W. Lord, "Coal," Geological Survey of Ohio, *Bull.* 9, 4th Lines, 268 (1908).

² S. W. Parr, Illinois State Geological Survey, *Bull.* 16, 212 (1909).

and size of the largest lumps of impurities and the quantity of original sample that can be taken without incurring too great a cost. The accuracy of any method of sampling should be frequently tested by taking two or more independent samples which are reduced and analyzed separately. Ordinarily the sample sent to the laboratory will weigh from three to five pounds, and will be pulverized to about $\frac{1}{4}$ inch size. The original gross sample which may amount to 500 or 1000 pounds must be pulverized, mixed and quartered in such a manner as to maintain the same relative proportions of coal and impurities until the final 3- to 5-pound sample is obtained; furthermore, coal has a marked tendency to lose moisture in crushing. This must be avoided as much as possible.

The final sample should be placed in a moisture-proof container for shipment to the laboratory. Wooden boxes or sacks should never be used for samples in which moisture is to be determined.

ACCURACY OF MINE SAMPLING

During the past nine years the Technologic Branch of the U. S. Geological Survey and its successor, the Bureau of Mines, has analyzed a large number of mine samples of coal, taken in connection with the investigation of coal as it occurs in the mine. These samples are taken by cutting down a section or groove of uniform cross section across the face of the seam. The gross sample, amounting to about six pounds for each foot in thickness of the coal bed, is pulverized to pass a $\frac{1}{2}$ inch screen, mixed and quartered down to about three pounds, which is placed in a galvanized iron can, sealed moisture-tight, and mailed to the laboratory.

In taking these samples some uniform system of including and rejecting the partings or bands of impurities that occur in coal beds is essential. Usually partings more than $\frac{3}{8}$ of an inch thick and lenses or concretions of "sulfur" or other impurities more than two inches in maximum diameter and $\frac{1}{2}$ of an inch thick are excluded. By following such a system the analytical results are comparable in representing the quality of coal in different coal beds; it is quite necessary to complete the sampling and seal the sample can at the face as quickly as possible after breaking down the coal in order to avoid loss of moisture.

These mine samples usually represent a better quality of coal than is ordinarily shipped from the mine, as in the operation of a mine it is not practicable to use the same care in excluding partings and other impurities. They are of value in showing the quality of coal as it occurs in the seam, at the point of sampling; and the results are subject to the unavoidable variations due to including more or less of the partings and the errors in reducing the gross sample to three pounds. It is possible to practically eliminate the errors of reducing the gross sample by crushing the entire quantity of coal cut down from the face, to less than 4 mesh size, and then mixing and quartering to 3 pounds. However, such a procedure is of doubtful value on account of the greater errors resulting from

the inclusion of more or less of the partings in cutting down the section, especially where they tend to crumble from the action of the pick.

There is also to be considered the variation in the proportion of impurities in neighboring sections; the extent of this variation is usually greater than the errors incurred in sampling the individual section.

In Table V are shown the results of a series of duplicate 3-pound can samples that were taken by the standard method of the Bureau of Mines as described in *Technical Paper 1*.¹

The entire sample which had been cut from the face was crushed to pass a $\frac{1}{2}$ inch screen, mixed and quartered to three pounds, which was called sample No. 1; the rejected portions were then combined, mixed and again quartered to three pounds, which was called sample No. 2. Both samples were sent to the laboratory in the usual galvanized iron sample cans, which are closed with a screw cap and made moisture-tight by wrapping the joint with electricians' tape. The samples were air dried, pulverized in the usual manner by rolls and ball mill and separately analyzed. The results obtained for total moisture, ash, and sulfur are given in the table.

TABLE V—A COMPARISON OF DUPLICATE 3-LB. SAMPLES TAKEN FROM THE SAME SECTION OF COAL

Location of mine	Total moisture			Ash			Sulfur		
	Sample 1 Per cent.	Sample 2 Per cent.	Difference Per cent.	Sample 1 Per cent.	Sample 2 Per cent.	Difference Per cent.	Sample 1 Per cent.	Sample 2 Per cent.	Difference Per cent.
Danville, Vermilion Co., Ill.									
Section A.....	12.4	12.4	0.0	7.8	7.9	0.1	2.9	3.0	0.1
Section B.....	13.1	13.2	0.1	10.0	9.9	0.1	4.0	3.5	0.5
Composite.....	12.8	12.7	0.1	8.8	8.8	0.0	3.5	3.2	0.3
Westville, Vermilion Co., Ill.									
Section A.....	13.3	13.2	0.1	8.5	9.2	0.7	2.3	2.4	0.1
Section B.....	15.3	15.5	0.2	7.9	8.0	0.1	1.6	1.7	0.1
Section C.....	16.2	16.2	0.0	8.2	8.3	0.1	1.8	1.8	0.0
Section D.....	14.8	14.9	0.1	8.7	8.5	0.2	1.9	2.0	0.1
Section E.....	15.5	15.4	0.1	7.1	8.7	1.6	1.5	2.8	1.3
Section F.....	15.2	15.1	0.1	8.6	8.7	0.1	2.9	2.9	0.0
Composite.....	15.1	15.1	0.0	8.2	8.5	0.3	2.1	2.3	0.1
Georgetown, Vermilion Co., Ill.									
Section A.....	15.2	15.1	0.1	9.8	9.7	0.1	2.0	2.1	0.1
Section B.....	15.4	15.5	0.1	11.2	10.9	0.3	1.9	1.9	0.0
Section C.....	15.9	15.7	0.2	11.6	12.2	0.6	2.4	2.6	0.2
Composite.....	15.5	15.5	0.0	10.9	11.0	0.1	2.1	2.2	0.1
Danville, Vermilion Co., Ill.									
Section A.....	13.1	13.0	0.1	10.0	9.8	0.2	3.2	3.1	0.1
Section B.....	12.9	12.8	0.1	9.3	9.3	0.0	3.7	3.5	0.2
Section C.....	12.7	12.7	0.0	9.7	9.6	0.1	3.7	3.4	0.3
Section D.....	12.6	12.5	0.1	9.1	8.8	0.3	3.1	2.9	0.2
Section E.....	13.9	13.8	0.1	9.1	9.7	0.6	3.1	2.8	0.3
Section F.....	13.8	13.8	0.0	8.5	8.5	0.0	2.9	3.0	0.1
Composite.....	13.0	13.1	0.1	9.3	9.2	0.1	3.2	3.2	0.0
Fairmont, Vermilion Co., Ill.									
Section A.....	14.2	14.1	0.1	9.6	9.9	0.3	2.2	2.3	0.1
Section B.....	13.6	13.5	0.1	9.1	9.8	0.7	2.1	2.3	0.2
Section C.....	13.4	13.1	0.3	11.3	11.4	0.1	2.6	2.8	0.2
Composite.....	13.7	13.6	0.1	10.0	10.4	0.4	2.3	2.4	0.1
Steeltown, Vermilion Co., Ill.									
Section A.....	15.9	15.8	0.1	10.7	10.3	0.4	2.4	2.6	0.2
Section B.....	14.2	14.2	0.0	9.9	10.0	0.1	2.2	2.5	0.3
Section C.....	14.9	14.6	0.3	8.5	8.7	0.2	2.3	2.5	0.2
Composite.....	15.0	14.8	0.2	9.8	9.7	0.1	2.3	2.5	0.2

¹ Method of taking mine samples is described in detail in Bureau of Mines, *Technical Paper 1*, "Sampling Coal in the Mine," by J. A. Holmes.

¹ J. A. Holmes, "Sampling Coal in the Mine," Bureau of Mines, *Technical Paper 1*.

TABLE V—Continued

Location of mine	Total moisture			Ash			Sulfur		
	Sample 1 Per cent.	Sample 2 Per cent.	Difference Per cent.	Sample 1 Per cent.	Sample 2 Per cent.	Difference Per cent.	Sample 1 Per cent.	Sample 2 Per cent.	Difference Per cent.
DuQuoin, Perry Co., Ill.									
Section A.....	10.4	10.7	0.3	9.6	9.0	0.4	0.8	0.8	0.0
Section B.....	11.5	11.6	0.1	8.7	9.0	0.3	0.8	0.9	0.1
Section C.....	10.7	10.9	0.2	10.6	10.8	0.2	0.9	1.0	0.1
Section D.....	10.5	10.6	0.1	12.2	11.7	0.5	1.0	0.9	0.1
Section E.....	10.1	10.3	0.2	11.6	11.8	0.2	0.9	0.8	0.1
Section F.....	10.8	10.7	0.1	11.0	11.5	0.5	0.8	0.8	0.0
Composite.....	10.7	10.7	0.0	10.7	10.6	0.1	0.9	0.9	0.0
Bruceton, Allegheny Co., Pa., Pittsburgh bed									
Section A.....	2.9	2.8	0.1	5.7	5.6	0.1	1.1	1.1	0.0
Section B.....	3.0	3.0	0.0	6.0	5.8	0.2	1.2	1.2	0.0
Section C.....	2.8	2.7	0.1	5.1	5.2	0.1	1.0	1.1	0.1
Section D.....	2.7	2.7	0.0	5.5	5.7	0.2	1.2	1.2	0.0
Composite.....	2.8	2.8	0.0	5.6	5.6	0.0	1.1	1.1	0.0
Colver, Cambria Co., Pa., Miller or "B" Bed									
Section A.....	5.4	5.2	0.2	1.0	1.0	0.0
Section B.....	4.9	4.7	0.2	0.9	0.9	0.0
Section C.....	5.1	5.2	0.1	1.0	1.0	0.1
Composite.....	5.1	5.0	0.1	1.0	1.0	0.0

	Moisture Per cent.	Ash Per cent.
Maximum difference in duplicate mine samples taken in Illinois.....	0.3	1.6(a)
Maximum difference in samples taken in Pennsylvania.....	0.1	0.2
Average difference in samples taken in Illinois.....	0.1	0.3
Average difference in samples taken in Pennsylvania.....	0.05	0.16

(a) Next highest difference in Illinois samples was 0.7.

On account of the high percentages of moisture, ash and sulfur and the irregular distribution of the impurities in the seam, Illinois coals are unusually difficult to sample. Yet in spite of the high moisture content, the greatest difference of moisture in duplicate samples was only 0.3 per cent., with an average difference for the 30 sections of 0.1 per cent.

In the four sections in the experimental mine the maximum difference was 0.1 per cent. and the average difference was 0.05 per cent.

The average variation in ash of the duplicate samples from seven sections in two Pennsylvania mines is 0.1 per cent.; the maximum variation being 0.2 per cent.

In the Illinois series the average ash variation is 0.3 per cent. and the maximum variation is 1.6 per cent.; the next highest difference is 0.7 per cent.

In an investigation of the quality of coal in the mine several samples should be taken at different places. These may be separately analyzed or combined at the laboratory into a composite sample. The composite analysis of several samples is subject to smaller sampling errors than the individual samples. For example, in Table V the largest ash variation in the composite analyses of samples Nos. 1 and 2 is 0.4 per cent., although several individual pairs of duplicate samples showed 0.7 per cent. difference and one pair out of the 36 had a difference of 1.6 per cent.

SAMPLING IN THE LABORATORY

Next in importance to securing a representative

sample to send to the laboratory, is the further treatment in the laboratory sampling room by which a representative powdered sample is obtained for analysis.

In the method used by the Bureau of Mines, moisture loss is avoided by air drying the 3-pound sample before pulverizing. The amount of moisture expelled during the air-drying process is recorded and added to the final moisture obtained by drying the powdered sample at 105° C. (221° F.). The air-dry sample is quickly pulverized to 10 mesh by passing through a roll crusher, reduced on a riffle sampler to about 450 grams (1 pound) and ground to 60 mesh in a moisture-tight ball mill which consists of rotating porcelain jars containing well-rounded flint pebbles. The final powdered sample is preserved in a rubber-stoppered bottle to prevent change in moisture content.

This method of sampling was developed by Lord and Somermeier at the U. S. Fuel Testing Plant at St. Louis. Numerous experiments have shown that this method reduces the unaccounted for moisture changes during sampling and analysis to a lower point than any other practicable method that has yet been devised. The very uniform moisture results obtained on the duplicate mine samples of the high moisture Illinois coals cited in Table V could not have been obtained by the old methods of pulverizing on a bucking board where the exposure of finely divided coal to a dry or humid atmosphere could change its moisture content.

Usually the laboratory sampling error with respect to ash, by the method just described, is less than 0.3 per cent. and seldom greater than 0.5 per cent. Where careful work is done by the sampler the 0.5 per cent. limit should not be exceeded. In Table VI are given some results of duplicate sampling, as illustrating the usual errors.

TABLE VI—A COMPARISON OF MOISTURE AND ASH IN DUPLICATE 3 OZ. POWDERED SAMPLES MADE FROM THE 3-LB. SAMPLES RECEIVED AT THE LABORATORY

Laboratory No.	Per cent. moisture in air-dry coal			Per cent. ash in air-dry coal		
	Sample A	Sample B	Difference	Sample A	Sample B	Difference
14807	1.95	2.02	0.07	12.93	12.78	0.15
14808	2.11	2.09	0.02	12.52	12.53	0.01
14809	6.90	6.81	0.09	13.40	13.12	0.28
14812	1.89	1.91	0.02	12.55	12.70	0.15
14813	0.92	0.92	0.00	6.10	6.36	0.26
14814	0.66	0.69	0.03	8.45	8.32	0.13
14815	3.57	3.67	0.10	16.64	16.27	0.37
14817	1.14	1.22	0.08	15.36	15.49	0.13
14818	1.63	1.65	0.02	10.63	10.47	0.16
14819	1.08	1.19	0.11	9.00	8.83	0.17
Average difference.....			0.05			0.18
Maximum diff. in 10 samples...			0.11			0.37

PREPARATION OF LABORATORY SAMPLE WITHOUT PRELIMINARY AIR DRYING

Where the highest degree of accuracy with respect to moisture is not required and where the analyses must be had in the shortest possible time, the method used in the inspection laboratory of the Bureau of

Mines will give satisfactory results.¹ This method consists in rapidly crushing the coarse sample to 20 mesh by means of a roll crusher or coffee mill type of grinder and taking a representative portion of this product for the determination of total moisture. The remainder and main portion of the sample is then mixed and divided with a riffle sampler to not less than 150 grams, which is then pulverized to 60 mesh with any suitable apparatus, such as a bucking board or disc pulverizer, without regard to moisture losses. Both samples are preserved in rubber-stoppered bottles.

The moisture determined in the 20 mesh sample represents the total moisture in the coal as received; the moisture in the final powdered sample is also determined in order to recalculate the analysis to the "as received" condition.

The results for moisture obtained by this method are somewhat low, due to unavoidable loss while crushing the coal to 20 mesh size. Wet coals must be partially air-dried and the loss of weight noted.

INCORRECT METHODS OF PREPARING COAL SAMPLES

The determination of total moisture by drying a portion of the coarse sample in a steam oven at about 105° C. (221° F.) will give low results, the error increasing with the size of the lumps.

The method of drying the coarse sample at temperatures above 100° C. (212° F.) and then pulverizing to a powdered sample for analysis, with the assumption that the powdered coal is dry coal, will give quite erroneous results. The powdered sample will never be dry but will contain from 0.3 to 1.0 per cent. moisture which it has either failed to give up while drying in the coarse condition, or has taken up from the atmosphere, while being pulverized. The heating values are directly effected by the errors in the sampling and in the moisture determinations.

ABRASION IN BALL MILLS

In using any apparatus for pulverizing samples the amount of contamination from abrasion of the pulverizing surfaces should always be investigated. Before the U. S. Fuel Testing Plant at St. Louis adopted the ball mill for the final grinding of coal samples, tests were made to determine whether there was danger of materially increasing the ash content of the samples from chipping and abrasion of the flint pebbles used in grinding. In these tests the weight of the sample ground each time on the ball

TABLE VII—LOSS(a) IN WEIGHT OF THREE LOTS OF FLINT PEBBLES USED FOR PULVERIZING COAL IN THE BALL MILL

Lot	Total weight of samples ground Grams	Loss by abrasion			
		Weight of pebbles		actual ground Grams	Ratio to coal ground Per cent.
		before grinding Grams	after grinding Grams		
No. 1 (250 samples ground)	125,000	4118.6	4113.1	5.5	0.004
No. 2 (230 samples ground)	115,000	3502.9	3499.4	3.5	0.003
No. 3 (245 samples ground)	122,500	4273.2	4268.3	4.9	0.004

(a) "Experimental Work of Chemical Laboratory, U. S. Fuel Testing Plant, St. Louis, Mo.," by N. W. Lord, U. S. G. S., *Bull.* 323, 8.

mill was approximately 500 grams, and the abrasion of the pebbles (calculated as percentage of the weight

(a) "The Fuel Inspection Laboratory of the Bureau of Mines," by J. D. Davis, Bureau of Mines, *Bull.* 41, 74 (1912).

of the samples ground) was determined from the loss in weight sustained by the pebbles. The results on these weighed lots of pebbles are shown in Table VII.

The results show only 0.004 per cent. increase in ash due to the abrasion from the pebbles.

In order to determine the extent of abrasion from the porcelain jar, the following tests were made:

TABLE VIII—LOSS IN WEIGHT OF PORCELAIN JARS USED FOR PULVERIZING COAL IN THE BALL MILL

	Total weight of sample ground Grams	Weight of jar		Loss by abrasion	
		before grinding Grams	after grinding Grams	actual Grams	Ratio to coal ground Per cent.
Jar No. 35 (100 samples of 150 grams each ground)...	15000	8095	8085	10.0	0.066
Jar No. 37 (100 samples of 150 grams each ground)...	15000	8317	8314	3.0	0.020
Jar No. 35 (100 samples of 300 grams each ground)...	30000	8085	8075	10.0	0.033
Jar No. 37 (100 samples of 300 grams each ground)...	30000	8314	8310	4.0	0.013
Jar No. 36 (30 samples of 300 grams each ground).....	9000	10789	10788	1.0	0.011

Evidently there is a little more abrasion from the porcelain jars than from the pebbles. In the experiments the same amount of material was abraded in 150-gram samples as in 300-gram samples, hence the necessity of using large samples: 500 grams is the best amount and should not cause the ash content to be raised more than 0.04 per cent. at the highest, which is less than the analytical error in the determination of ash.

A more direct test of added ash from abrasion was made by placing 400 grams of ordinary granulated sugar in the mill and rotating it continuously for four hours. Before grinding, the sugar contained 0.04 per cent. ash; after grinding, it contained 0.06 per cent. ash—an increase of 0.02 per cent.

That the ball mill is the most satisfactory appliance for pulverizing coke is shown by the following experiments: Ten samples of a hard foundry coke weighing about 25 lbs. each were crushed to 10-mesh size by first passing through a chipmunk jaw crusher and then through a pair of steel rolls. Each sample was then mixed and divided with a riffle into three portions of about 8 lbs. each. The first portion was again put through the rolls until all of the 8 pounds passed through a 20-mesh sieve, and was then mixed and reduced with the riffle to 150 grams which was rubbed down to 60 mesh on a chilled cast iron bucking board. The second 8-pound portion of each sample was also put through the rolls again until all passed the 20-mesh sieve; was then riffled down to 150 grams and pulverized to 60 mesh in a tool steel diamond mortar. The third 8-pound portion of each sample was mixed and divided on the riffle to about 300 grams, which was then placed in the ball mill and pulverized to 60 mesh. Owing to the extreme hardness of this coke, 4 hours rotation in the ball mill was required to pulverize to 60 mesh. After removing from the ball mill the entire sample was put through the 60-mesh sieve, mixed and reduced on the riffle to about 60 grams for analysis.

All the 60-mesh samples were tested for iron with

TABLE IX. ASH IN COKE PULVERIZED BY THREE DIFFERENT METHODS

Laboratory No.	Difference in ash found in				
	Ash in sample pulverized with bucking board	Ash in sample pulverized with diamond mortar	Ash in sample pulverized with ball mill	bucking board and ball mill	diamond mortar and ball mill
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
11033	12.9	11.8	11.8	1.4	0.3
11034	12.9	11.4	10.8	2.1	0.6
11035	12.8	10.3	10.5	2.3	0.2
11036	15.2	11.3	10.8	4.4	0.5
11037	..	10.0	9.7	..	0.3
11038	..	10.7	10.7	..	0.0
11039	..	11.8	10.6	..	0.2
11040	15.4	12.3	10.9	4.5	1.4
11041	..	10.3	10.1	..	0.2
11042	..	10.2	9.7	..	0.5
Average...					0.4

a magnet. No magnetic particles were found in the ball-mill sample and only a few in the diamond-mortar sample; the bucking-board sample showed the presence of considerable metallic iron. Ash determinations were made on each of the diamond-mortar and ball-mill samples and on some of the bucking-board samples. The results are shown in Table IX.

With only one exception the samples pulverized in the ball mill contained the least ash; the diamond mortar, which crushes by impact, ranks second. Rubbing surfaces of chilled iron and even chrome steel, such as used in the bucking board and disc pulverizer, are abraded by the hard particles of coke, and, therefore, should never be used for the fine grinding of coke.

CONCLUSIONS

To state definite limits of accuracy for coal analyses is almost impossible. The factors which influence the results are many and variable. They depend on the kind and quality of coal, the method of sampling and analysis, and the skill and experience of the analyst in the special field of coal testing.

With the exception of the volatile matter, fixed carbon and oxygen determinations, the best analytical methods are more accurate than the usual methods of sampling. The method of taking the original sample is often limited by the commercial conditions. The determination of the heating value with the use of properly standardized calorimeters and thermometers is reliable and comparable. Appreciable errors, when such occur, are generally due to sampling or a change in the composition of the sample by oxidation or loss of moisture. Finally, a statement of how the sample was taken should always go with the report of analysis. This will enable one who has a knowledge of coal to properly interpret the report of analysis.

U. S. BUREAU OF MINES
PITTSBURGH

THE EFFECT OF CERTAIN PIGMENTS ON LINSEED OIL; WITH A NOTE ON THE MANGANESE CONTENT OF RAW LINSEED OIL¹

By E. W. BOUGHTON

Received February 19, 1913

At the time the Contracts Laboratory of the Bureau of Chemistry was making some exposure tests on painted

¹ Published by permission of the Secretary of Agriculture.

steel plates some of the mixtures of various pigments of known composition with raw linseed oil of known analytical constants were set aside in closed jars of uniform shape and size in order to learn what changes would take place in the oil upon standing. No drier was added to these samples. The paints were so prepared that after the addition of drier they had approximately the same viscosity, 47 to 50 (water = 6.2), as determined by a Stormer viscosimeter. The jars were stoppered air-tight and placed in a closet having a glass door, where the light was dim and diffused.

The following table gives the list of pigments that were used and the proportions, by weight, of pigment and oil.

TABLE I—COMPOSITION OF PAINTS

Pigment	Pigment by weight Per cent.	Oil by weight Per cent.	Pigment	Pigment by weight Per cent.	Oil by weight Per cent.
White lead (basic carbonate).....	72	28	Artificial graphite	42	58
Kaolin (contains CaSO ₄).....	50	50	Zinc white (American chromate).....	39	61
Indian red.....	50	50	Chrome yellow (lead)	34	66
Flake graphite.....	40	60	Chromium oxid, green	51	49
Magnetic oxid, black(a)	46	54	Lampblack.....	16	84
Zinc yellow (zinc chromate).....	45	55			

(a) Analysis by H. C. McNeil: Loss at 110° C., 0.56 per cent.; Na₂CO₃, 2.82 per cent.; FeCO₃, 18 per cent.; Fe₂O₄, 60.4 per cent.; Fe₂O₃, 18.3 per cent.

At the end of one- and two-year periods the contents of each jar were well mixed and a portion poured out, thinned with ether, and centrifuged. After decanting the supernatant liquid from the pigment the greater part of the ether was evaporated on the steam-bath, and the oil heated for half an hour at 105° C. in an inert gas, carbon dioxide being used for the one-year and hydrogen for the two-year samples. The last traces of pigment were removed by filtering through fine filter paper. The black pigments settled with difficulty. The oil extracted from the lampblack paint was red and muddy and was not analyzed. Judging from its constants, appearance, and odor, the linseed oil purchased in the open market was undoubtedly unadulterated. The constants were as follows:²

Specific gravity (15.6° C.)	0.934	Iodin number.....	179.6
Saponification number.....	193.6	Ash (per cent.).....	0.13
Acid number.....	1.7	Unsaponifiable matter (per cent.).....	0.68

Unfortunately all the oil was used in making the paints, so that the changes which would have occurred in keeping it without pigments could not be noted. It has been proved, however, that raw linseed oil kept in glass away from bright sunlight for two years does not change appreciably with respect to its analytical constants, except for a slight rise in acid number.²

As the different pigments settled with different degrees of compactness in the jars, the surface of contact was larger in some cases than in others. Since the contents of the jars were mixed before sampling, the change in analytical figures as obtained repre-

¹ Analysis by E. M. Dawson.

² Proc. Amer. Soc. Test. Mat., 11, 197 (1911).

sents an effect upon the total volume of oil. The results are shown in the following table:

Pigment	Time of exposure Years	Specific gravity (15.6° C.)	Iodin number	Ash Per cent.	Color
White lead (basic carbonate)	{ 1 2	0.940 0.938	175.8 177.3	0.35 0.40	Bleached "
Kaolin	{ 1 2	0.939 0.936	173.0 171.6	0.12 0.14	Very much bleached
Indian red	{ 1 2	0.941 0.939	173.8 172.5	0.15 0.14	Bleached "
Flake graphite	{ 1 2	0.934 0.933	180.9 178.2	0.21 0.15	Normal "
Magnetic black	{ 1 2	0.937 0.935	174.6 173.2	0.17 0.13	" "
Zinc yellow	{ 1 2	0.934 0.934	180.2 179.5	0.20 0.18	" "
Artificial graphite	{ 1 2	0.935 0.939	181.0 180.8	" 0.15	" "
Zinc white	{ 1 2	0.935 0.934	181.3 179.7	0.25 0.13	" "
Chrome yellow	{ 1 2	0.937 0.935	176.3 175.7	0.14 0.14	Bleached "
Chromium oxid, green	{ 1 2	0.937 0.937	178.0 180.2	0.01 0.05	" "
Original oil		0.934	179.6	0.13	

Before commenting on the figures it may be well to discuss the general action of pigments on linseed oil. Toch¹ stated that the hydrolysis of the glycerids in linseed oil by moisture is hastened by the presence of lime or lead salts. White lead, sublimed lead, and zinc oxid all showed the same bleaching power within two weeks, irrespective of the kind of raw linseed oil used. Slow chemical reactions take place between the lead and zinc pigments and the oil. Painters sometimes prefer a white-lead paste which is old. Toch also stated that the iodine number of a pure raw linseed oil may be reduced to 110 by the addition of metallic salts, as Japan drier, but this statement does not mean that such a large reduction is caused by the reaction between pigment and oil.

Sabin² emphasized the strong action of litharge upon linseed oil and stated that the effect of red lead (Pb₃O₄) on oil may be due to the litharge content, as, by preparing a red lead from litharge in the form of an impalpable powder, thus securing practically complete oxidation to the higher oxids of lead, the product is without the usual action when mixed with oil. A mixture of white lead and oil dries more rapidly than oil alone, but so small is this increase that it is not recognized in practice. In the drying process the action of the inert pigments, asbestine, China clay, etc., is similar to that of white lead, which may be due to physical rather than chemical causes. In fact, no pigments are really inert to oil with respect to the drying process, and this pigment action is of great value in paint.

Klein³ stated that linseed oil extracted from paint is frequently found to have a low iodine number and quoted Boettinger's⁴ experiments which showed a reduction of the iodine number from 183.3 to 131 by white lead in 17 days, and to 122.2 in two months. Whiting and ocher showed the same changes. In the original article, however, Boettinger stated that

the mixtures of oil and pigments were exposed to light and air, so that it was in reality a study of the effect of pigments on the amount of atmospheric oxidation of the oil.

Gardner¹ made mixtures of pigments and linseed oil, using very small quantities, and, after allowing them to stand, determined the increase in the amount of ash. Zinc oxid, white lead, and red lead were the only pigments that gave an appreciable increase in the amount of ash.

In a later paper² he gave the results of allowing linseed oil to stand in contact with different pigments for two years. Although the experiments were similar to those reported in this paper, the results were very different. The pigments that Gardner used were zinc oxid, basic carbonate of lead, combinations of lead and zinc pigments, barytes, silica, basic chromate of lead, red lead, iron oxid, carbon black, and graphite. The iodine number of the original oil was 181. The samples extracted from the pigments had iodine values varying from 135 to 163. The specific gravity was greatly raised by silica and iron oxid and slightly by most of the others. The pigments containing lead and zinc caused an increase in the amount of ash, showing actual chemical combination. Where the other constants were greatly changed the acid number of the oil was much raised. Gardner called attention to the fact that the combination of pigment and oil is due to hydrolysis with the formation of free fatty acid. The determination of this increase, therefore, is of importance as showing to what degree the glycerid has been broken up, thus increasing its tendency to combine with the pigment. In the case of the mixture of oil and silica, hydrolysis took place, as shown by the high acid number, but the pigment did not go into solution. The viscosity of the mixtures, being slightly greater than that ordinarily found, is doubtless somewhat in excess of that of the paints listed in Table I.

As Gardner stated that in two of his jars a skin was formed upon the surface, it seems probable that air entered into the reaction. This may be the cause of the difference in the results. Again, if an oil containing certain metals in solution is heated in air to drive off the last traces of solvent, oxidation will occur in a short time.

TABLE III—IODIN NUMBERS OBTAINED BY HEATING OIL UNDER DIFFERENT CONDITIONS

Oil	Gas used	Time of heating		Iodin number		Oil	Gas used	Time of heating		Iodin number
		Hours						Hours		
A	Air	2		173		C	Air	2		174
	Hydrogen	2		182			Air	4		168
	Carbon dioxide	2		180			Hydrogen	2		177
B	Air	2		158			Hydrogen	4		177
	Air	4		143			Carbon dioxide	2		178
	Carbon dioxide	2		180			Carbon dioxide	4		179
	Carbon dioxide	4		174						

The need of using an inert gas when heating oils extracted from paint is illustrated by the figures in Table III. Oil A, extracted from a white-lead paste, contained some dissolved lead. The iodine number of the fatty acids was 185. Oil B was prepared by

¹ "The Chemistry and Technology of Mixed Paints," 1907.

² Bottler and Sabin, "German and American Varnish Making," 1912.

³ Allen, "Commercial Organic Analysis," (4th Ed.) p. 336, 1910.

⁴ Chem. Ztg., 22, 102, 558 (1898).

¹ "Paint Technology and Tests," 1911.

² J. Frank Inst., 174, 1912.

dissolving lead linoleate in pure raw linseed oil. The amount of lead in solution was 3.23 per cent., and the iodine number of the prepared oil was 177. Oil C was a pure raw linseed oil having an iodine number of 179. The oils were dissolved in ether, and, after distilling off the bulk of the ether, were heated at 98° to 99° C.

In order to have the iodine number furnish reliable information regarding the nature of the oil used in a paint, it is necessary to saponify and separate the fatty acids, making the determination on them. As the iodine number of the fatty acids is about 4 per cent. greater than that of the glycerid, the lower limit for oil from North American seed is about 185 and from South American seed about 178.

Gardner stated that "when paints are stored for a considerable length of time and then examined for the iodine value of their oil content, a lowering of the iodine value should not constitute cause for rejection or be sufficient evidence that the oil was adulterated with oils of lower iodine value." This is still open to question, as the results of the work in the Contracts Laboratory indicate that but little change takes place during two years. The changes that occur in a closed paint can are naturally very different from those in a drying paint film. Although not yet shown to be true, it is probable that in the latter case under the influence of light, air, and moisture there is actually more chemical combination between pigment and oil. An oil showing a high acid number has more effect upon a pigment that is basic in its nature, such as white lead, than an oil with a very low acid number as that used for this work.

The results in Table II show that the iodine number is in no case reduced sufficiently to place it below a figure frequently given by samples of pure raw linseed oil. Since duplicate determinations of the iodine number often vary as much as two units, a difference not exceeding that must be disregarded in comparing the different samples. The lower limit for oil from North American seed is placed at 178,¹ from South American seed at 171.² In the Contracts Laboratory many samples from unknown sources, which have shown all the characteristics of pure raw oil, have had an iodine number of 170 to 172.

It is interesting to note that while the iodine number of the oil was changed only slightly in all the mixtures, a greater decrease was caused by so-called inert pigments, kaolin, and Indian red, than by the others which include the lead and zinc pigments.

The large amount of ash from the white-lead samples undoubtedly shows that some of the pigment has been actually dissolved by the oil. The other figures for ash, however, do not show with certainty that there has been an appreciable solution of pigment.

The specific gravity of the oil was raised slightly in almost every case, but as with the iodine number the effect of two years' exposure was practically the same as that of one year. The upper limit for raw oil is placed at 0.936 at 15.6° C.³ Many of

the extracted oils are slightly above that figure.

A rise in specific gravity may be caused by the solution of some of the metallic portion of pigment in the oil, by volatilization of a portion of the oil, or by oxidation. Oxidation would be accelerated by small amounts of dissolved lead, manganese, or other catalytic agents. As the oil after two years showed no increase in specific gravity over the one-year figure (except in one case), the air enclosed in the jar probably had very little effect. The samples of extracted oil were rather small for an accurate specific gravity determination, so that a difference of one or two units in the third decimal place must be disregarded.

Kaolin had greater bleaching effect than any of the other pigments, the black pigments and the zinc white causing practically no change in the color of the oil. The jars were filled completely, so that the influence of air must have been negligible for the first year. As a portion was removed at the end of that time, during the second year of exposure about 100 cc. of air filled the space above the paint in the jar.

The constants of an oil mixed with a pigment into a thick paste might be changed more than those of oil in the kind of paint used in these experiments, for a greater proportion, if not practically all, of the oil would then be in direct contact with the pigment. Samples of oil extracted from stiff white-lead pastes in this laboratory have yielded fatty acids with an iodine number of 185. The nature and original constants of the oils were unknown. The addition of driers and thinners would also influence these constants, and the results of these experiments are comparable only with paints made exclusively of raw oil and pigment in such proportions that the paint is ready for use without thinning.

Although the effect of white lead upon the specific gravity and iodine number is, under these circumstances, practically no greater than that of some of the other pigments, it is evident from the amount of ash that a greater weight of the pigment has gone into solution, though, considering the higher atomic weight of lead, the extent of chemical action need be no greater. The lead chromate did not combine with the oil to so great an extent as the basic carbonate.

The tendency of some of the pigments is to increase slightly the specific gravity of the oil, in many cases raising it above the higher limit for pure raw linseed oil, 0.936; hence a figure obtained on the extracted oil which is near the lower limit for pure raw linseed oil, 0.932, may indicate the presence of other oils of lower specific gravity.

NOTE ON THE MANGANESE CONTENT OF RAW LINSEED OIL

In 1911 sixteen samples of raw linseed oil of known purity and source were sent out to the members of the Subcommittee on Linseed Oil of the American Society for Testing Materials. Voorhees¹ found manganese in the ash of all the samples. In the Contracts Laboratory the same oils were ashed and the amount of manganese determined. Thirty grams of oil were

¹ *Proc. Amer. Soc. Test. Mat.*, **9**, 164 (1909).

² *Ibid.*, **11**, 202 (1911).

³ *Proc. Amer. Soc. Test. Mat.*, **9**, 164 (1909).

¹ *Proc. Amer. Soc. Test. Mat.*, **11**, 209 (1911).

used and the manganese determined by the bismuthate method. Table IV shows the results. The percentage of manganese is figured on the oil.

TABLE IV—MANGANESE CONTENT OF RAW LNSEED OIL

Ash		Manganese		Ash		Manganese	
Sample No.	Per cent.	Per cent.	Sample No.	Per cent.	Per cent.	Sample No.	Per cent.
1.....	0.16	0.0004	9.....	0.19	0.0008		
2.....	0.02	0.0005	10.....	0.21	0.0006		
3.....	0.03	Faint trace	11.....	0.05	Faint trace		
4.....	0.16	0.0005	12.....	0.03	Faint trace		
5.....	0.03	Faint trace	13.....	0.03	0.0005		
6.....	0.18	0.0003	14.....	0.04	Faint trace		
7.....	0.18	0.0002	15.....	0.16	0.0005		
8.....	0.16	0.0003	16.....	0.16	0.0003		

CONTRACTS LABORATORY
BUREAU OF CHEMISTRY
WASHINGTON, D. C.

PINE NUT OIL

By MAXWELL ADAMS AND AUGUST HOLMES

Received January 3, 1913

The nut pine tree, *Pinus Monophylla*, also known as *Pinus Fremontiana*, Pinon Pine and Grey Pine, according to Heller¹ grows along the eastern slopes of the Sierra Nevada Mountains from Steamboat Springs on the North to Lower California on the South. It varies in height from a mere shrub, on the borders of the desert, to a magnificent tree almost a hundred feet in height, in the Tehachapi Mountains. On the middle scale of the cones of this tree is borne an oblong thin-shelled seed about 15 mm. in length and weighing about one gram. The color of the nut is yellowish on the upper surface and dark reddish brown on the lower. The endocarp is resinous and oily, possessing a rich and pleasant taste.

Capt. John C. Fremont,² who first discovered this species of pine, in January, 1844, near the present site of Carson City, Nevada, states that the nuts from this tree constituted the principal subsistence of several Indian tribes, whom he visited during his explorations in the Great Basin. At the present time the Indians still gather the nuts in large quantities; a part is sold in the local markets, the remainder is used by the Indians for food.

The nuts used in the following experiments were gathered from trees growing on the mountains west of Walker Lake, Nevada, in the Autumn of 1911. A routine analysis of the nut kernels gave the following results:

	Air-dry Per cent.	Green Per cent.	Water free Per cent.
Water.....	7.88	61.57	
Ash.....	2.60	1.08	2.82
Ether extract.....	22.77	9.49	24.70
Crude fiber.....	0.65	0.27	0.70
Crude protein.....	8.94	3.73	9.70
Nitrogen-free extract.....	57.21	23.86	62.08
Nitrogen.....	1.43	0.59	1.55

About eight kilograms of the nuts were partially air dried, hulled, the kernels ground and the oil extracted with ether in a Jacobson extractor.³ The nuts used in one extraction gave the following yield:

Weight of nuts used.....	522 grams
Weight of kernels obtained.....	400 grams
Weight of oil extracted.....	65 grams
Per cent. of oil in nuts.....	12.4
Per cent. of oil in kernels.....	16.2

¹ Muhlenbergia, 5, 335.

² Fremont's First and Second Expeditions, p. 221.

³ Jour. Am. Chem. Soc., 23, 2052.

The oil obtained from the evaporation of the ether extract is of the consistency of ordinary olive oil and at first is light yellow in color, but upon standing in the laboratory the color gradually fades. A sample which remained near a window for a year became entirely colorless. The oil has a pleasing aromatic odor and agreeable taste. Blasdale¹ reports that a sample, bought in the open market, and supposed to be pine nut oil, examined by him, had a disagreeable odor and rancid taste. The oil in question must have been extracted from stale nuts, or obtained from the nuts of some pine other than *Pinus Monophylla*, for the physical constants, determined by him, differ markedly from those obtained by us, when examining the freshly extracted oil.

The oil melts at -15° , turns brown and decomposes without boiling at 320° , but when heated under a pressure of 60 mm. it begins to distill without decomposition at 305° . The saponification value, determined by the method of Kottstorfer, is 189.31, and the iodine absorption value, when determined by the method of Hübl, gives the following results:

	Expt. I	Expt. II
Weight of oil used.....	0.2466	0.2338
Weight of iodine absorbed.....	0.2663	0.2525
Iodine value.....	107.97	108.00

The refractive index, determined with an Abbé refractometer, is as follows:

Temperature Degrees	Refractive index
10	1.4747
15	1.4733
20	1.4716
25	1.4698
30	1.4680
35	1.4662
40	1.4543

The refractive index, saponification value and iodine number of the oil, which had been bleached in the sunlight, was determined but no change was noted, except that the iodine number showed a slight diminution, which is probably due to the absorption of oxygen by the semidrying oils present.

The oil was submitted to fractional distillation, at a pressure of 60 mm., and each fraction examined with the refractometer, in order, if possible, to separate it into distinct chemical compounds, with the following results: 150 cc. of the oil were used for fractionating.

Fraction	Temperature Degrees	Vol. of distillate Cc.	Ref. index at 40°
1	305	0.5	1.4522
2	305-15	20	1.4531
3	315-20	50	1.4550
4	320-50	30	1.4562
5	350-65	20	1.4570
6	365-70	5	1.4594

At 320° the oil in the distilling flask turns brown and begins to show signs of decomposition, which increases as the temperature rises. At the end of the experiment there is in the flask a black tar-like residue. The first three fractions are liquids, the last three solids, at room temperature. The change in the refractive index and the variation in the melt-

¹ Jour. Am. Chem. Soc., 17, 935.

ing points indicate a difference in the composition of the several fractions, but when they were submitted to a second distillation they showed no tendency to produce substances with definite boiling points, and each decomposed somewhat when distilled and left a residue of tar.

The glycerine in the oil was determined by oxidizing with potassium permanganate in alkaline solution, according to the method of Benedikt and Zsigmondy,¹ and found to be 9.2 per cent.

When 200 grams of the oil, dissolved in alcohol, are saponified with potassium hydroxide, and evaporated to dryness, to free the residue from alcohol, it dissolves readily and completely in water, to a clear solution. This test indicates the absence of phytosterol.

The mixed fatty acids when precipitated from the soap solution with dilute sulfuric acid, washed and dried, are light yellow in color, have a sp. gr. of 0.904 at 15°, and the yield is about 90 per cent. of the total oil. The mixed acids, when separated by treating their slightly alcoholic solution with lead acetate, according to the method of Gusserow-Varrentrap,² yielded 82 per cent. of unsaturated acids and 8 per cent. of saturated acids. This method does not give exact quantitative results as Lewkowitsch³ has already pointed out, and the following iodine value determination shows that the saturated acids thus obtained are impure:

	Expt. I	Expt. II
Weight of saturated acid used. . . .	0.4054	0.3844
Iodine number.	6.6	6.5
Weight of unsaturated acid used. . .	0.4016	0.3782
Iodine number.	116.8	117.1

0.6031 gram of these mixed saturated acids was dissolved by warming with 100 cc. of alcohol, sp. gr. 0.91, which had previously been saturated with pure stearic acid at 0° C., and allowed to stand in a flask surrounded by ice water for twenty-four hours. The white, laminated crystals which separated were filtered from the solution and weighed when dry 0.0657 gram. Their melting point was 66°. This yield shows the presence of 10.8 per cent. stearic acid in the mixed saturated acids, or about 1 per cent. stearic acid in the original oil.

Using the iodine number of oleic acid as 90.07, and the iodine number of the impure saturated acids, determined above, as 6.6 in the following equation 100×6.6
 90.07 = per cent. oleic acid, we have
 7.21 per cent. oleic acid present. Assuming that the impure saturated acids obtained by the lead salt method consisted wholly of stearic, palmitic and oleic acids, there would be, calculated by difference, 82 per cent. palmitic acid present in the saturated acids. There was, however, obtained by the crystallization from alcohol of the magnesium salt of the mixed saturated acids, a very small yield of an acid, which had a refractive index of 1.4236 at 72°. This is identical with that given by Partheil and Ferrie⁴ for lauric acid. The

quantity available was not sufficient for a more complete identification.

The unsaturated acids obtained are light yellow in color, have a sp. gr. at 15° of 0.938 and have a refractive index as follows:

Temperature Degrees	Refractive index
15	1.4657
20	1.4635
25	1.4623
30	1.4604
35	1.4588
40	1.4570
45	1.4550

The neutralization value of the mixed unsaturated fatty acids is 211.1, and the mean molecular weight calculated from this data is 265.7.

Oleic acid, according to the investigations of Hazura,⁵ is converted into hydroxystearic, and linolic acid into sativic acid, when the mixed acids are oxidized with potassium permanganate in dilute alkaline solution. After oxidizing ten grams of the mixed acids by this method, the acids were recovered by passing into the solution a stream of sulfur dioxide, until the solution had an acid reaction. The precipitated acids were then collected on a filter and separated by extracting the hydroxystearic acid in a Soxhlet apparatus with ether. The solution thus obtained was evaporated to a small volume and cooled, where the white laminated crystals of dihydroxystearic acid separated. The crystals thus obtained after a second recrystallization had a melting point of 132°. The dihydroxystearic acid obtained was 44 per cent. of the total unsaturated acids, which corresponds to 39.2 per cent. oleic acid. This method does not give quantitative results, since a considerable amount of the dihydroxystearic acid remains in the ether solution, used for extraction and purification, but it serves to fix the lower limit for the amount of oleic acid present.

The residue remaining in the Soxhlet apparatus which was insoluble in the ether, was extracted repeatedly with hot water, and the sativic acid allowed to crystallize. The ten grams of mixed fatty acids used gave 0.8 gram of a white crystalline substance having a melting point of 171°, which is slightly lower than that given for tetrahydroxystearic acid. Were the acid pure this corresponds to 6.4 linolic acid. Besides the oleic and linolic acids the presence of small quantities of other unsaturated acids were indicated, but no confirmatory tests made were successful in proving their identity. Assuming that the mixed fatty acids consisted entirely of oleic and linolic acids, calculated from the following formula,

$$\begin{array}{r} x + y = 100 \\ 90.07x \pm 181.42y = 117.05 \\ 100 \qquad \qquad 100 \end{array}$$

where x equals the per cent. of oleic, y equals the per cent. of linolic acid, and 117.05 the iodine number of the mixed acids, there would be present 70.5 per cent. of oleic and 29.5 per cent. of linolic acid. But by the method of Hazura we obtain only 6.4 per cent. of linolic acid. Experimental errors and inaccuracies of the two

¹ Jour. Soc. Chem. Ind., 1885, 610.

² Liebig's Ann., 27, 153; 35, 197.

³ Jour. Soc. Chem. Ind., 1890, 845

⁴ Archive. der Pharm., 1903, 545.

⁵ Mond. f. Chemie, 1887, 147-260.

methods do not satisfactorily account for so great a variation in results. Careful tests by the method of Hazura failed to show the presence of linolenic acid, but from the high iodine absorption, some unidentified unsaturated acid appears to be present.

From these experiments we conclude that the oil from the nuts of *Pinus Monophylla* consists chiefly of the glyceride of oleic acid together with small amounts of the glycerides of stearic, palmitic, lauric and linolic acids.

CHEMICAL LABORATORY
UNIVERSITY OF NEVADA
RENO

ANALYSES OF CERTAIN OF THE PACIFIC COAST KELPS¹

By E. G. PARKER AND J. R. LINDEMUTH

Received February 5, 1913

While many kinds of kelp are to be found on both the Atlantic and Pacific coasts, the giant kelps, peculiar to the Pacific coast, are the most important to the United States from an economic standpoint because of their size and remarkable content of potassium salts. While the other varieties grow from two to twelve feet in length, the giant kelps are found from 30 to 200 feet in length, and in specific cases much longer.

The composition of the Pacific kelps was studied first by David M. Balch,² of Coronado Beach, California. He analyzed specimens of the giant kelps of the northern and southern Pacific coast of the United States, including *Nereocystis luetkeana*, *Macrocystis pyrifera*, and *Pelagophycus porra*. Later in the course of an investigation of the fertilizer resources of the United States, under the direction of Dr. Frank K. Cameron,³ the composition was studied by Dr. J. W. Turrentine,⁴ of this Bureau, who analyzed specimens of various algae collected from Alaska by Mr. E. C. Johnston, of the "Albatross," from Puget Sound (San Juan County), Washington, by Prof. Geo. B. Rigg, of the University of Washington; from the region of Monterey Bay, California, by Prof. F. M. McFarland, of Leland Stanford Jr. University; and from the vicinity of San Diego, California, by Capt. W. C. Crandall, of the La Jolla Marine Biological Station.⁵ From these analyses it has been concluded that the genres are, in the north—the *Nereocystis luetkeana* and *Macrocystis pyrifera*, and in the south—the *Macrocystis pyrifera* and the *Pelagophycus porra*; also, that the indications are that the northern kelps are richer in potassium chloride than the southern.

Samples.—Specimens of *Macrocystis pyrifera* and *Nereocystis luetkeana* were collected for analysis in Freshwater Bay, Washington, by Prof. George B. Rigg: from 34°–38° N, 120°–124° W, and also from 32°–33° N, 117°–118° W, by Capt. W. C. Crandall. The samples collected by Prof. Rigg were shipped dry, in glass jars, while those by Capt. Crandall were shipped dry, in canvas bags. In each case the entire

sample was dried at 103° C. until it would easily powder, and was then ground, care being taken not to lose any of the adhering salts, or salts shaken off into receptacle in transit. After grinding, the whole sample was mixed well to ensure homogeneity.

Method of Analysis.—The methods of analysis used were in the main those employed by Turrentine.⁴ The results of the analyses are recorded in Table I, p. 288.

The determinations of nitrogen were made by Mr. T. C. Trescott, of the Bureau of Chemistry, to whom we are greatly indebted. The determinations were made on the oven-dried samples by the Kjeldahl method. The locations from which samples were collected by Crandall are given in latitude and longitude. A detailed description of this work by Crandall and Rigg, together with a complete set of working charts of the Pacific kelp groves from Puget Sound southward, will soon be published by the Bureau of Soils.

DISCUSSION OF ANALYTICAL DATA

In the second column are given the serial numbers of the kelp samples examined. There are three series consisting of three collections of samples secured during the year 1912. They are designated by the initial letter of the name of the collector: as R, Rigg, C, Crandall, C', Crandall (different collection).

An inspection of Table I (see p. 288) results in the following averages:

TABLE II

	KCl Percent.	I Percent.	N Per cent
Series R (aver. of 11).....	27.63	..	2.14
Series C (aver. of 19).....	23.84	..	2.21
Series C' (aver. of 9).....	10.34	..	1.11
Macrocystis (aver. of 23).....	15.82		
Nereocystis (aver. of 16).....	30.50		
Series R (Mac) (aver. of 2).....	19.47		
Series R (Ner) (aver. of 9).....	29.54		
Series C (Mac) (aver. of 12).....	19.20		
Series C (Ner) (aver. of 7).....	31.74		
Series C' (Mac) (aver. of 9).....	10.54		
Entire table (aver. of 39).....	21.85	0.20	1.93

From Tables I and II the following conclusions may be drawn:

1. That the average potassium chloride content is high.

2. That apparently no definite relation exists between the different constituents of kelp.

3. That the total average potassium chloride content of the *Nereocystis luetkeana* is greater than that of the *Macrocystis pyrifera* and that for the potassium chloride content of kelp from different localities the same is true; also that in every case the potassium chloride content of the *Nereocystis luetkeana* is greater than the average potassium chloride content of the *Macrocystis pyrifera*.

4. That apparently the northern kelps are richer in potassium chloride than the southern.

5. That the kelp from the southern coast of California (Series C', Table II) is comparatively low in potassium chloride. The fact that the average potassium chloride content of kelp from the same locality was found to be much higher both by Balch and Turrentine, and also that the nitrogen content is

¹ Published by permission of the Secretary of Agriculture.

² Balch, THIS JOURNAL, 1, 177 (1909).

³ Senate Doc. No. 190, 62nd Congress, 2nd Session, 1912.

⁴ Turrentine, THIS JOURNAL, 4, 431 (1912).

⁵ Now the Scripps Marine Biological Station, of the University of California.

¹ Turrentine, loc. cit.

TABLE I

Serial No.	Name of kelp	Location	Description	Potash	Iodine	Nitrogen	Sol. salts	Organic	Ash	KCl
				(K ₂ O) Per cent	(I Per cent.	(N Per cent.	(Na, K, Cl, SO ₄) Per cent.	matter Per cent.		
1 R1	Nereocystis luetkeana	Freshwater Bay	Fronds	18.04	0.23	2.26	44.17	51.13	4.80	28.56
2 R2	Nereocystis luetkeana	Freshwater Bay	Fronds	17.61	0.24	2.21	44.17	51.11	4.72	27.87
3 R3	Nereocystis luetkeana	Freshwater Bay	Stipes	31.62	0.25	1.21	63.75	33.15	3.46	50.05
4 R4	Nereocystis luetkeana	Freshwater Bay	Fronds	16.92	0.20	2.57	43.31	51.16	5.47	26.76
5 R5	Nereocystis luetkeana	Freshwater Bay	Fronds	17.05	0.24	2.71	41.53	51.67	6.30	26.98
6 R6	Nereocystis luetkeana	Freshwater Bay	Fronds	17.32	0.28	2.53	45.40	50.12	4.48	27.40
7 R7	Nereocystis luetkeana	Freshwater Bay	Fronds	16.20	0.19	2.54	42.88	52.14	4.98	25.64
8 R8	Nereocystis luetkeana	Freshwater Bay	Stipes	16.50	0.30	2.21	59.24	37.40	3.36	26.13
9 R9	Nereocystis luetkeana	Freshwater Bay	Stipes	16.72	0.20	1.46	57.06	39.02	3.92	26.44
10 R10	Macrocystis pyrifera	Near Law Point	Fronds	11.82	0.22	2.43	28.32	67.78	3.90	18.70
11 R11	Macrocystis pyrifera	Near Law Point	Stipes and pneumatocysts	12.80	0.23	1.37	34.42	59.40	6.18	20.23
				14.17	0.24	2.15	33.40	62.95	3.64	22.40
12 C1	Macrocystis pyrifera	34°-28'-20"								
		120°-28'-50"								
13 C2	Macrocystis pyrifera	34°-31'-10"		9.35	0.25	2.72	20.25	73.06	6.69	14.78
		120°-31'-30"								
14 C3	Macrocystis pyrifera	35°-9'-30"		8.62	0.14	2.35	23.14	68.26	8.60	13.63
		120°-42'-30"								
15 C4	Nereocystis luetkeana	35°-10'-35"		20.83	0.24	1.93	49.06	47.86	3.08	32.99
		120°-48'-40"								
16 C4a	Nereocystis luetkeana	35°-10'-35"		19.71	0.25	1.96	53.50	43.02	3.48	31.18
		120°-48'-40"								
17 C5	Macrocystis pyrifera	35°-26'-10"		4.14	0.19	2.40	13.95	82.17	3.88	6.55
		120°-35'-0"								
18 C6	Macrocystis pyrifera	35°-37'-30"		6.06	0.15	2.68	14.24	79.66	6.10	9.60
		121°-13'-30"								
19 C7	Macrocystis pyrifera	36°-56'-25"		12.26	0.18	3.17	30.52	63.28	6.20	19.39
		120°-5'-45"								
20 C8	Macrocystis pyrifera	36°-57'-30"		12.38	0.18	2.11	28.02	68.79	3.19	19.58
		122°-8'-0"								
21 C9	Macrocystis pyrifera	37°-6'-0"		16.44	0.24	2.16	35.88	59.80	4.32	26.02
		122°-17'-40"								
22 C10	Macrocystis pyrifera	37°-56'-30"		9.52	0.18	2.38	23.90	72.37	3.73	15.07
		122°-46'-0"								
23 C11	Nereocystis luetkeana	38°-49'-0"		16.72	0.13	2.22	43.32	53.56	3.12	26.45
		123°-36'-30"								
24 C12	Nereocystis luetkeana	38°-51'-30"		20.62	0.15	2.25	45.48	51.42	3.10	32.63
		123°-40'-0"								
25 C13	Sample decayed									
26 C14	Macrocystis pyrifera	37°-56'-40"	Young plant	17.26	0.15	2.18	38.26	58.18	3.55	27.30
		122°-7'-0"								
27 C15	Macrocystis pyrifera	37°-56'-40"	Old plant	27.66	0.14	1.00	56.02	41.04	2.93	43.78
		122°-7'-0"								
28 C16	Macrocystis pyrifera	37°-66'-40"	Young on bottom of old plant	8.13	0.15	2.10	21.27	75.57	3.16	12.85
		122°-7'-0"		16.96	0.20	2.15	38.06	57.26	4.68	26.83
29 C17	Nereocystis luetkeana	36°-37'-50"	Old plant							
		121°-54'-52"								
30 C18	Nereocystis luetkeana	36°-37'-50"	Young plant	23.82	0.17	2.41	50.51	47.26	2.22	37.72
		121°-54'-52"								
31 C19	Nereocystis luetkeana	36°-37'-50"	Very old plant	21.70	0.18	1.58	46.60	50.20	3.20	34.35
		121°-54'-52"								
32 C'1	Macrocystis pyrifera	Imperial Beach near San Diego		6.68	0.27	1.93	23.12	67.47	9.40	10.57
33 C'2	Macrocystis pyrifera	Monument Bet. Mex. & U. S. Chart 5100		3.20	0.18	1.56	16.56	76.46	6.98	5.06
34 C'3	Macrocystis pyrifera	W. Descanso Pt. (Mex. territory)		6.33	0.23	1.52	19.51	77.17	3.32	10.02
35 C'4	Macrocystis pyrifera	S. Coronado Is. So. of island		7.98	0.14	1.81	23.69	67.72	8.60	12.61
36 C'5a	Macrocystis pyrifera	32°-51'-30"		7.18	0.22	0.64	20.34	76.50	3.16	11.35
		117°-17'-6"								
37 C'5b	Macrocystis pyrifera	32°-51'-30"		6.79	0.25	0.79	20.12	76.55	3.32	10.73
		117°-17'-6"								
38 C'5c	Macrocystis pyrifera	32°-51'-30"		6.39	0.24	0.66	18.62	77.78	3.60	10.10
		117°-17'-6"								
39 C'5d	Macrocystis pyrifera	32°-51'-30"		7.82	0.23	0.67	24.06	72.40	3.54	12.38
		117°-17'-6"								
40 C'5e	Macrocystis pyrifera	32°-51'-30"		6.50	0.22	0.54	22.22	74.86	2.92	10.28
		117°-17'-6"								

also correspondingly low, leads to the belief that these particular specimens do not fairly represent the kelps of that locality.

6. That the iodine content of northern and southern kelps show no conclusive differences.

Considering, now, all the results which have been obtained on the kelps of the Pacific coast, it is to be noted first that if Balch's ratio of sodium to potassium,

1 : 4, determined for *Pelagophycus porra* held also for *Macrocystis* and *Nereocystis*, the former would have an average of 35.45 and the latter 36.93 per cent. potassium chloride. While many individual samples would undoubtedly run as high or even higher than these figures, they are almost certainly too high as averages. Turrentine's results show that the northern *Macrocystis* (2 samples) contain 26.5 per

cent. and the Nereocystis (4 samples) 30.9 per cent. potassium chloride, the average for all being 29.4 per cent. The southern Macrocyctis (22 samples) contained 21.6 per cent. and the Nereocystis (2 samples) 35.9 per cent. or an average of 23.4 per cent. for 26 samples. Turrentine's results indicate that the northern Nereocystis contains somewhat less potassium chloride than the southern, while the reverse holds for Macrocyctis and the kelps as a whole.

The results obtained by the authors thus confirm the conclusions from Turrentine's analyses. Finally, disregarding the results of Balch, the average content of all samples so far examined give:

TABLE III

	North Per cent. KCl	South Per cent. KCl	Total Per cent. KCl
Nereocystis.....	28.1	32.7	31.1
Macrocyctis.....	23.0	20.8	21.0

BUREAU OF SOILS

U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

THE SPECIFIC HEAT OF COAL AND ITS RELATION TO THE PRESENCE OF COMBINED WATER IN THE COAL SUBSTANCE¹

By HORACE C. PORTER AND GUY B. TAYLOR

Received March 7, 1913.

The specific heat of coal is hardly capable of precise determination. Coal is a conglomerate of varying composition, unstable and easily subject to change by heat and by exposure to the air. Nevertheless, a determination of the specific heat is possible on a given sample with some degree of accuracy, and there may be determined also the influence of the character of the coal and the percentage of moisture on the specific heat.

When coal is being heated it passes ordinarily through a range of temperature from about 20° C. to 250° or 300° C. before it ignites, or before, in the absence of air, it begins to decompose rapidly by destructive distillation. During this preliminary heating of coal, whether in a coke oven, gas retort, or gas producer or in the "green" coal layer of a furnace fuel bed, it is of interest and often of value to fuel engineers to know the relative quantity of heat communicated to the coal for a given temperature rise, *i. e.*, its specific heat.

Solids have in general a much lower heat capacity than that of water, metals in most cases less than 0.1 and sand, fire clay, porcelain or glass not far from 0.2. These solid substances thus require only $\frac{1}{10}$ or $\frac{1}{5}$ as much heat as is required by water, in order to raise their temperature a given number of degrees. Coal we should expect, by reason of its organic nature and its content of water, to have a higher specific heat than metals or clay. Bituminous coal, air-dry, proves to have, in fact, through the temperature interval 28° to 65° C., a value varying from 0.261 for the New River type to 0.370 for Wyoming sub-bituminous of 11% moisture. The specific heat becomes greater at higher temperatures, that of the New River type, for example, being 0.354 between 177°

and 227°. In Table I are given the results of the determinations of specific heat made in this investigation.

Different authorities have given the specific heat of coal as varying from 0.20 to 0.45, with usually no qualifying statement as to moisture content or character of the coal. As a matter of fact, the moisture content materially affects the specific heat, and from the relationship between the specific heats of dry and undried coal may be deduced certain conclusions as to the combination of the water present.

TABLE I. SPECIFIC HEATS OF DIFFERENT COALS

k	W	dT	k	specific heat, W	weight of water heated + water	W	dT	k	Temp
	W	dT				W	dT		range, ° C
equivalent of apparatus (14.1 grams), k = weight of substance, dT = rise of temperature in calorimeter, dT = fall of temperature in coal									
Expt. No.	Coal No. or substance	W	W	w	dT	dT	k	Temp range, ° C	
39	9614 (New River).....	229.5	45.0	1.95	37.6	0.264	66.0	28.4	
44	9614 (New River).....	238.6	40.0	1.56	36.0	0.259	64.0	28.4	
45	9614 (New River).....	206.7	40.0	1.74	34.4	0.261	62.8	28.6	
49	384 (Pittsburg).....	215.6	40.0	1.85	34.8	0.286	63.5	28.6	
50	384 (Pittsburg).....	204.8	39.1	1.71	31.8	0.282	60.8	29.0	
51	384 (Pittsburg).....	209.4	40.0	1.80	32.9	0.286	61.8	28.9	
52	384 (Pittsburg).....	223.1	40.0	1.67	32.2	0.289	61.6	29.0	
27	48 (Illinois).....	236.8	40.0	2.07	35.3	0.347	61.4	29.1	
28	48 (Illinois).....	246.8	40.0	1.90	35.0	0.335	64.4	29.0	
29	48 (Illinois).....	249.5	40.0	1.98	36.4	0.339	64.4	28.4	
32	48 (Illinois).....	220.9	40.0	2.16	34.7	0.344	63.0	28.9	
36	48 (Illinois).....	218.8	39.9	2.04	33.6	0.333	62.5	28.3	
37	48 (Illinois).....	232.6	34.9	1.77	34.4	0.343	62.9	28.5	
59	48 (in toluene) (a).....	122.5	35.0	2.97	31.4	0.331	61.5	30.1	
61	48 (in toluene).....	123.3	28.8	2.56	32.0	0.342	61.0	29.0	
72	575 (Wyoming).....	208.6	30.0	1.97	36.2	0.378	63.9	27.7	
73	575 (Wyoming).....	232.2	40.0	2.40	37.2	0.374	63.4	26.2	
74	575 (Wyoming).....	242.2	26.5	1.71	38.5	0.375	64.2	25.7	
66	575 (in toluene).....	123.8	30.0	2.96	32.9	0.371	62.2	29.3	
67	575 (in toluene).....	123.2	25.0	2.47	33.8	0.361	63.2	29.4	
76	575 (in toluene).....	124.7	30.0	3.11	36.2	0.357	62.4	26.2	
62	48 (dry).....	123.3	30.0	2.46	33.4	0.302	62.8	29.4	
63	48 (dry).....	122.3	30.0	2.44	33.1	0.301	62.6	29.4	
64	48 (dry).....	122.3	28.0	2.30	33.5	0.300	62.7	29.2	
68	575 dry.....	122.6	30.0	2.62	34.3	0.312	63.8	29.3	
69	575 (dry).....	124.1	25.0	2.26	35.2	0.318	64.3	29.1	
15	Copper (c).....	218.5	103.1	1.58	35.9	0.0933	64.6	28.7	
19	Copper.....	227.3	107.1	1.49	35.7	0.0933	64.8	29.1	
17	Copper.....	227.4	102.2	1.53	36.5	0.0933	64.7	28.2	
41	Copper.....	196.3	101.3	1.70	38.3	0.0933	63.5	28.2	
14	Lead (0.0310 at 17°-100°) (d).....	237.1	284.6	1.35	36.4	0.0308	64.5	28.1	
3	Same.....	210.1	356.0	1.84	35.7	0.0305	64.3	28.0	
23	Marble (0.206 at 0°-100°) (d).....	235.8	60.0	1.88	36.8	0.201	64.8	28.0	
24	Same.....	232.6	60.0	1.68	36.4	0.202	64.8	28.4	
33	Jena glass (0.2182 at 18°-99°) (d).....	209.8	14.5	1.35	33.1	0.192	61.5	28.4	
40	Same.....	197.2	52.6	1.93	36.7	0.197	66.2	29.5	
(a) Water equivalent of toluene = weight used ÷ 0.421									
(b) Using toluene.									
(c) Used as standard, to determine water equivalent of calorimeter, assuming specific heat as 0.0933. In expt. 15, 204.3 grams of water were used; in No. 19, 215.3, in No. 17, 212, and in No. 41, 183.4 grams									
(d) Values taken from Landolt and Börnstein Tabellen.									

Table I. SPECIFIC HEATS OF COALS AT HIGHER TEMPERATURES
 Water equivalent of calorimeter 14.1 grams

Expt. No.	Coal No. or substance	W	α	dT	dt	t	Temp. range, °C
90	Copper	201.7	48.0	2.03	100.4	0.0933	128.8-28.1
102	Copper	209.1	48.0	2.11	103.8	0.0948	129.8-28.7
98	884	216.7	10.0	1.48	106.1	0.302	131.0-24.9
100	881	224.1	12.0	1.53	108.1	0.307	130.0-24.9
101	881	226.6	11.0	1.63	104.6	0.313	130.0-28.4
108	884	193.2	10.0	1.68	104.6	0.310	130.0-28.4
103	9614	222.7	11.0	1.48	103.3	0.290	128.0-24.7
104	9614	208.1	10.0	1.43	102.3	0.287	127.8-25.2
106	9614	191.8	9.8	1.81	106.2	0.287	132.0-28.8
88	Copper	340.2	41.0	1.73	181.3	0.0948	176.0-24.7
90	Copper	324.8	37.0	1.67	188.9	0.0938	181.0-25.1
92	Copper	318.1	36.7	1.68	184.1	0.0936	179.0-24.9
89	384	313.1	10.0	1.57	183.3	0.318	178.5-24.2
96	384	320.9	10.0	1.48	148.0	0.321	172.7-24.7
93	9614	314.8	12.0	1.76	184.8	0.298	179.0-24.5
94	9614	308.0	10.0	1.49	181.8	0.303	176.0-24.5
108	Copper	296.9	20.0	1.24	198.4	0.0942	220.7-28.3
110	Copper	296.9	30.0	1.90	198.3	0.0948	223.7-28.4
107	384	330.5	6.0	1.22	200.1	0.332	225.5-28.4
109	384	307.1	8.0	1.73	199.8	0.332	225.5-28.7
111	9614	314.1	8.0	1.64	204.6	0.315	229.7-28.1
113	9614	278.0	9.0	2.03	201.0	0.312	226.6-28.6

Table II—SUMMARY OF AVERAGE VALUES OBTAINED FOR THE SPECIFIC HEAT OF COAL AT DIFFERENT TEMPERATURES

Coal	CALCULATED VALUES					
	63°-28°	130°-25°	177°-23°	227°-23°	130°-63°	177°-130°
9614	0.261	0.288	0.301	0.314	0.303	0.329
384	0.286	0.308	0.320	0.332	0.321	0.347
48	0.339					
48 (dry)	0.301					
575	0.370					
575 (dry)	0.318					

the air. In other words, the vapor pressure of the moisture in coal does not reach the normal tension of water vapor until the amount present exceeds a certain percentage; up to that percentage, therefore, the water present in coal does not exist as free superficial moisture. An experimental study of the vapor tensions of coals of different water content, bringing them to equilibrium over sulfuric acid of various dilutions, has confirmed these conclusions.¹

By comparison of the specific heats of dry and undried coal, knowing the percentage of water present, the molecular heat of the water may be calculated. A coal from Franklin Co., Illinois, bearing 8.4 per cent. water, has a specific heat of 0.337, while in the dry condition its value is 0.301. Following Kopp's law, the specific heat of the water present in this coal is $0.337 - (0.916 \times 0.301) = 0.730$, and its molecular

heat, $18 \times 0.730 = 13.1$. Similarly a Wyoming subbituminous of 11.0 per cent. moisture has in the undried condition a specific heat of 0.359 and in the dry state 0.315, the specific heat of its water being thus

$$0.359 - (0.89 \times 0.315) = 0.718$$

and the molecular heat

$$12.9$$

The molecular heat of the combined water in many hydrated salts has been determined by Kopp and others.² Some examples are given below:

TABLE II

Substances	% H ₂ O	Specific heat	Molecular heat of water present
CuSO ₄ 5H ₂ O (Schottky)	36.1	0.269	8.6
CuSO ₄ (anhydrous) (Schottky)		0.151	
MgSO ₄ 7H ₂ O (Kopp)	51.2	0.407	10.6
MgSO ₄ (anhydrous) (Kopp)		0.216	
BaCl ₂ 2H ₂ O (Schottky)	14.7	0.151	9.1
BaCl ₂ (anhydrous)		0.090	
MnSO ₄ 5H ₂ O (Kopp)	37.4	0.407	14.1
MnSO ₄ (anhydrous) (Kopp)		0.182	
Coal 48 (Ill.)	8.4	0.337	13.1
Coal 48 (dried)		0.301	
Coal 575 (Wyo.)	11.0	0.359	12.9
Coal 575 (dried)		0.315	

The molecular heat of the water in coal is evidently lower than that of free uncombined water and approaches that of the combined water of some crystallized salts. The conclusion therefore follows, in agreement with that drawn from the vapor-pressure relationships, that the moisture of coal is in part physically or chemically combined. Still further experimental evidence of the presence of combined water was incidentally encountered in developing the method for the determination of specific heat. In attempting to determine the value for dry coal by the method of mixtures, adding the heated coal to water in a calorimeter, so large a rise of temperature resulted that the specific heat appeared to be much greater than that of the undried coal. Since moisture should increase the specific heat of coal on account of the higher specific heat of water even when in combination, the discrepancy was at once attributed to some inherent error of the method. This error was found to lie in the development of heat by the physical or chemical action of water on the dry coal. Dry coal and water carefully brought to the same temperature in separate vessels were mixed in a calorimeter and the development of heat measured. The results given in Table III show in case of the Wyoming coal No. 43 a heat development of 20.0 calories per gram. In the specific heat determination using 30 grams of this coal dry, and mixing it with water, there were developed 600 calories therefore, as heat of combination, affecting in no small degree the result of the specific heat determination.

The values for the specific heat of dry coal were therefore determined by using toluene in place of water in the calorimeter, since toluene was found to have almost no calorific action on the dry coal. That the calorific action of water on dry coal is due to chemical or physical combination becomes highly probable in the light of the two other phenomena previously mentioned which point to the same conclusion, viz., the low vapor pressure and the low molecular heat of the water in coal.

¹ Acknowledgment is due to Mr. O. C. Ralston for the greater part of the experimental work on vapor pressure of coal.

² Kopp, *Phil. Trans. London*, **155**, [1] 71 (1865); Schottky, *Zeit. phys. Chem.*, **64**, 415 (1908); Jackson, *J. Am. Chem. Soc.*, **34**, 1470 (1912).

TABLE III—HEAT OF COMBINATION, DRY COAL AND WATER
(Water equivalent of calorimeter + water = 48 grams.)

Expt No	Coal No.	Wt. of coal.	Wt. of dried coal	Original moisture, per cent.	Moisture in dried coal	Temp rise, Deg. C.	Total calories	Calories per gram original coal	Calories per gram dried coal
2a	43	15.0	11.93	20.4	1.0	4.31	207.0	13.8	17.3
2b	43	15.0	12.00	20.0	1.4	3.97	191.0	12.7	15.9
3a	43	15.0	11.80	21.6	0.0	4.92	236.0	15.7	20.0
3b	43	15.0	11.80	21.3	0.1	4.79	230.0	15.3	19.5
4a	43	15.0	14.43	3.8	17.6	0.40	19.2	1.3	1.4
b	43	15.0	13.98	6.8	14.6	0.69	33.5	2.2	2.4
c	43	15.0	13.31	11.3	10.1	1.21	58.0	3.9	4.3
d	43	14.5	12.50	14.0	7.4	1.79	86.0	5.9	6.8
e	43	15.0	12.09	19.4	2.0	3.55	170.4	11.4	14.1
f	43	15.0	11.92	20.5	0.9	4.36	209.0	13.9	17.5
5a	43	..	14.00	...	16.7	0.36	17.3	...	1.2
b	43	..	14.00	...	14.8	0.45	21.6	...	1.5
c	43	..	14.00	...	14.8	0.46	21.7	...	1.5
11	43	..	14.00	...	15.1	0.53	25.4	...	1.7
7a	48	15.0	14.70	1.98	6.7	0.16	7.7	0.51	0.52
b	48	15.0	14.43	3.79	4.9	0.20	9.6	0.65	0.66
c	48	15.0	14.23	5.18	3.5	0.36	17.3	1.15	1.22
d	48	15.0	14.04	6.38	2.3	0.58	27.8	1.85	1.99
e	48	15.0	13.86	7.60	1.1	0.66	31.7	2.11	2.30
f	48	15.0	13.75	8.32	0.4	1.08	51.8	3.45	3.80
g	48	15.0	13.70	8.62	0.1	1.21	58.1	3.90	4.20
8	48	15.0	13.77	8.25	0.5	0.98	47.0	3.13	3.33
9a	384	15.0	14.82	1.20	0.6	0.12	5.7	0.39	0.40
b	384	15.0	14.78	1.44	0.4	0.18	8.6	0.57	0.58
10a	9614	15.0	14.84	1.05	0.1	0.0	0.0
b	9614	15.0	14.85	0.98	0.2	0.08

EXPERIMENTAL METHODS

Experimentally, the determinations of specific heat were carried out as follows: Early in the work an attempt was made to use a method depending upon the addition by electrical means of a definite amount of heat energy to coal suspended in water, noting the rise of temperature which resulted in the coal and water mixture. Since, by this method, using a weight of coal a little more than one-tenth that of the water, the total energy change of the system was 30 times that of the coal, the experimental error was magnified 30-fold when referred to the coal. Thus, in order to obtain an accuracy of 3 per cent. in the final result, an accuracy of 0.1 per cent. was required in the experiment. This degree of precision being scarcely practicable, the simpler method of mixtures was resorted to, whereby it was possible to effect a comparatively large energy change in the coal itself. The coal was heated to a temperature about 37° above that of the calorimeter, and was subjected thus, on mixing with the water of the calorimeter, to a change of temperature of about 34°, while the water changed less than 3°. The total energy change in the coal was equal to that in the balance of the system or, in other words, one-half of that of the entire system, so that the experimental error became magnified only two-fold when referred to the coal. The determinations were easily checked with a maximum deviation of 2 per cent. from the mean (see Table I).

The calorimeter vessel was a tinned can of 400 cc. capacity resting on a cork in a large Dewar vessel more than twice the height of the can. The Dewar,

tube rested in a jar of water at room temperature. A revolving propeller-shaped stirrer was used, attached to a glass rod and operated by a water motor at 150–200 revolutions per minute. The thermometer was a calibrated Beckmann of good quality. For introducing the heated coal or other substance a wide glass tube—about 3/4 inch in diameter—was inserted from above so as to direct the fall of the coal properly, yet not touch the calorimeter can, stirrer, or liquid. The coal was sized between 10 and 20 mesh, so as to fall easily through the tube and mix with the water.

For the heating of the coal before mixing, a double-walled cylindrical glass vessel was used, between the walls of which a little methyl alcohol was kept boiling by a platinum coil electrically heated. The inner cylinder contained the coal, supported near the bottom by a metal plate which could be quickly pushed out, allowing the coal to drop. A calibrated thermometer graduated in tenths of a degree rested in the center of the coal in the inner tube. When the coal had reached a constant temperature, the heater was brought over the calorimeter and the coal dropped.

In order to correct for radiation, temperature readings were taken at one-minute intervals during a 5-minute period before the mixing and during a 10-minute period after the maximum temperature had been reached. The cooling correction was applied by the well-known Regnault method common in calorimetric work. The temperature rise due to the mixing reached its maximum usually in 3 minutes, and the cooling correction applied did not exceed 0.05° or about 2 per cent. of the total rise.

The amount of water used in the calorimeter was 200–230 grams; the water equivalent of the apparatus was determined by runs with pure copper shot assuming the specific heat of pure copper at 28°–67° to be 0.0933—an average of Naccari's values at 17° and 100°, and based also on Schmitz's value (0.0936) at 20°–100°. On this basis the specific heats of a number of other substances were determined in the apparatus, comparing the values obtained with those given by other authorities, and the agreement was found good in most cases (see Table I).

Determinations were made upon four coals of widely varying character, two being high-grade Eastern coals of low moisture content and two from the Interior and Western fields comparatively high in moisture content. They were used both in the air-dry and the moisture-free condition, but not in the unstable moist condition as received from the mine. The moisture-free samples were prepared by drying 100 grams, 10–20 mesh size, for two hours in a 30 mm. vacuum at 100° C.

For the determinations upon dry coal, toluene was used in place of water. The water equivalent of the apparatus containing toluene was redetermined with copper. Some of the determinations made on undried coal in water were repeated in toluene and the agreement was good (see Table I).

¹ See Landolt and Bornstein's Tables, 4th Ed., and the original papers of Naccari. *Atti di Torino*, **23**, 10, 1888; Schmitz, *Proc. Roy. Soc.*, **72**, 177, 1903.

TABLE IV. DESCRIPTION OF COALS

Lab. No.	Source	Loss on	Analysis of air-dried sample			
		air drying	Moisture	Vol. matter	Fixed carbon	Ash
9614	Sun Mine, Fayette Co., W. Va. (New River field)	2.0	1.80	20.38	2.36	8.46
384	Schoenberg Mine, Baird Station, Washington Co., Pa. (Pittsburgh bed)	1.1	1.20	31.80	38.44	8.86
48	Dering No. 11 Mine, W. Frankfort, Ill. (Franklin Co.)	3	8.40	34.98	48.23	8.42
575	Dietz No. 2 Mine, Sheridan Co., Wyo. (sub-bituminous)	14.0	11.00	38.86	40.24	10.20
* Not determined; sample allowed to dry at 20°-25° in air of room.						

The specific heats of two coals (9614 and 384) were determined at higher temperature ranges, *viz.*, 130° to 25°, 177° to 25°, and 227° to 25° (see Table Ia). For preheating the coal there was used a mercury bath heated to the desired temperature and a double-walled glass test tube for transferring the heated coal from the bath to the calorimeter. A thermometer was imbedded in the coal while it was being heated, and temperature read immediately before dropping the coal, correction being made for the exposed stem of the thermometer. About 10 grams of coal were used. The determinations were checked by copper at each temperature. On account of the difficulty of avoiding loss of moisture during the preliminary heating, no determinations were attempted on the Illinois and Wyoming coals at these higher temperatures. Having the average specific heat between 25° and 63° and the average between 25° and 130°, it is possible to calculate the average value between 63° and 130°; similarly also those between 130° and 177° and between 177° and 227° (see Table Ib).

HEAT EVOLVED BY MIXING DRIED COAL AND WATER

For the approximate determination of the heat evolved by mixing dried coal with water, 12-15 grams of dry or partially dried coal of known moisture content were mixed with 40 cc. of water in a nickel calorimeter cup, and the mixture stirred by hand with the thermometer. The nickel cup rested on a cork in a deep Dewar vessel standing in a water bath. The thermometer was a calibrated Beckmann. The coal, before mixing with the water, was contained in a glass tube with movable bottom, and was brought to the temperature of the water by holding in an air bath of the right temperature until a thermometer imbedded in the coal became constant at the point desired. The tube of coal was then brought over the calorimeter cup and the coal dropped into the water by moving aside the supporting disc at the bottom.

With the Wyoming coal the maximum temperature was reached in 2-5 minutes, while with the Illinois coal the action was slower, requiring from 8 to 12 minutes to produce a maximum temperature. The cooling correction was small.

The water equivalent of the apparatus was determined by mixing two portions of water of different temperatures, and was also calculated roughly from the known specific heats of the materials. An aver-

age value of 4.5 grams was used. To this was added, in order to obtain the total heat capacity of the system, the weight of water used and an approximate value for the water equivalent of the coal used. The latter value, however, involved an uncertainty due both to the change in specific heat of the coal by combining with water and to the conversion of part of the free water into combined water of a different specific heat. The two errors tend to balance each other and the resultant error was probably not large. Taking 12.5 grams of dry coal, its water equivalent was assumed to be 3.7 grams with a probable error of 0.3 gram, or less than 1 per cent. of the total heat capacity.

The coals used were the same as in the specific heat determinations except that in place of the air-dried sample No. 575, an undried sample from the same mine, No. 43, containing 21.42 per cent. moisture, was substituted in order to observe the full effect of saturation of the coal substance with water. The coals were ground so as to pass a 20-mesh sieve and be retained on a 40-mesh. The moisture in them, determined by the official method of the Bureau of Mines,¹ was as follows:

No. 43	Sheridan Co., Wyo.	21.42%
No. 48	Franklin Co., Ill.	8.70
No. 384	Pittsburg bed, Pa.	1.78
No. 9614	New River district, W. Va.	1.15

There is an error due to oxidation in the official method for moisture determination, rendering the results for moisture content, especially in case of the Illinois and sub-bituminous Wyoming types, appreciably lower than the true percentage. Consequently no precise comparisons between heat developed and moisture content can be made from the results in Table III, since the moisture figures are not strictly accurate. The samples used in the determinations (see Table III) were prepared as follows:

Expts. 2, 3, and 4 (Coal 43): 15 gram portions dried for varying periods of time over sulfuric acid at 2 mm. pressure, determining loss of moisture by loss of weight and the moisture remaining by difference between this loss and the total moisture (official method).

Expt. 5: 15 grams of coal saturated with water and then air-dried at room temperature.

Expt. 11: Original coal, air-dried at room temperature 72 hours.

Expt. 7: (Coal 48), dried *in vacuo* over sulfuric acid as in Expt. 4.

Expt. 8: 15 gram portions in weighing bottle, oven-dried at 105°, 1½ hours in current of air.

Expts. 9 and 10: Coals 384 and 9614, dried *in vacuo*, as in Expt. 4.

SUMMARY

Coal has a specific heat varying according to the character of the coal substance and the amount of moisture, both free and combined, which the coal contains. The water content affects the specific heat in such manner as to indicate that up to a certain percentage the water is present in a state of physical or chemical combination. Other facts, *viz.*, the low vapor tension of the water in coal and the de-

¹ Techn. Paper, 8, U. S. Bureau of Mines, p. 5.

velopment of heat on moistening dry coal, support this theory. The heat development by the moistening of dry coal may contribute appreciably to the spontaneous heating of some coals in storage.

APPLICATION OF THE DIMETHYL SULFATE TEST FOR DETERMINING SMALL AMOUNTS OF PETROLEUM OR ASPHALT PRODUCTS IN TARS¹

By CHARLES S. REEVE AND RICHARD H. LEWIS

INTRODUCTORY

The recent production of mixtures of tar with various asphalt and petroleum products for use in the road and paving industry has necessitated a satisfactory method for determining the proportions of each type of material present in such mixtures. The authors have based their research on the well-known dimethyl sulfate test proposed by Valenta² and later investigated and reported upon by Graefe³ and Harrison and Perkin.⁴ A. Sommer⁵ modified the test in order to render it applicable for the estimation of asphalt in tar-asphalt mixtures, and Chapin⁶ now uses it in a modified form for the detection of adulterants in coal tar creosote sheep dips. A brief review of the literature upon the test to date will, therefore, prove of value, before submitting our data.

THE DIMETHYL SULFATE TEST

Valenta's purpose in originating the test was to determine the amount of tar oils present as an adulterant in paraffin and rosin oils, and he claimed as a result of his investigations that while aromatic hydrocarbons are freely miscible with dimethyl sulfate, the open-chain hydrocarbons are entirely insoluble in that reagent. It was, therefore, only necessary to thoroughly agitate a measured volume of the sample under examination with a measured volume of dimethyl sulfate, and the increased volume of the latter would indicate the amount of aromatic hydrocarbons which had gone into solution. This is in general, but not absolutely, correct, and the real facts regarding the test as brought out by later investigations are briefly summed up by Chapin as follows:⁷

- "1. Aromatic hydrocarbons and derivatives thereof are completely soluble in dimethyl sulfate, being miscible in all proportions.
- "2. Open-chain hydrocarbons show varying degrees of solubility in dimethyl sulfate, ranging from zero to a considerable percentage, light oils as a rule being the more soluble.
- "3. Treatment of a mixture of aromatic and open-chain hydrocarbons with dimethyl sulfate results in the formation of two layers; the upper contains most of the open-chain hydrocarbons plus a varying but usually small amount of aromatic hydrocarbons retained in solution; the lower layer contains practically all of the dimethyl sulfate, holding in solution most of the aromatic hydrocarbons plus a varying

but usually small amount of the open-chain hydrocarbons.

"The test, therefore, is no absolutely quantitative one, as indeed is to be expected from the laws of solubility. Results obtained thereby may, however, under favorable circumstances, closely approach quantitative values, and so may prove very useful for practical work."

In order to make the test applicable to solid and semi-solid bitumens which could not be directly treated with the reagent, A. Sommer¹ proposed distilling the sample to coke.

"Four cc. of the distillate obtained are then put in a ten cc. graduated cylinder with ground glass stopper and six cc. of dimethyl sulfate are added and shaken thoroughly for one minute. If the distillate is not entirely soluble, separation takes place within a few minutes and a separating mark can be accurately read. The percentage of solubility is calculated from this reading."

His results show that not only the open-chain hydrocarbons but also the distillates from native bitumens—largely polymethylenes—are insoluble in dimethyl sulfate. A mixture of 20 per cent. tar and 80 per cent. asphalt yields a distillate which is 15 per cent. soluble in the reagent, while a mixture of 80 per cent. tar and 20 per cent. asphalt yields a distillate which is 60 per cent. soluble. These are the extreme proportions reported upon by him. The authors, upon attempting to detect 10 per cent. of asphalt in several tar asphalt mixtures, failed to get any indication of its presence by this method, and since some current specifications provide for smaller proportions than 10 per cent., the necessity for a more delicate modification of the method gave rise to the following research.

EXPERIMENTAL

A consideration of the conditions involved in Sommer's method of operation led us to the obvious conclusion that when 10 parts of a hard oil asphalt is fluxed with 90 parts of a fluid coal tar, the total distillate obtained by destructively distilling such a mixture to coke would contain but a very small percentage of anything but aromatic hydrocarbons. Since it is known, and will be again demonstrated, that such distillates are slightly soluble in dimethyl sulfate, such a small percentage in a 4 cc. sample might not be recognized. It was, therefore, thought probable that the procedure suggested by Chapin, *i. e.*, to work on separate fractions of high boiling point, might lead to our finding a fraction in which the proportion of other hydrocarbons to aromatic hydrocarbons would be sufficiently large to permit of the former being easily detected. In order to determine just which fractions might prove of most value, several varieties of products which are being used in tar-asphalt mixtures were first distilled and their higher boiling fractions tested by means of dimethyl sulfate in the method prescribed by Sommer. The distillation was made in an 8-ounce glass retort with the top of the thermometer bulb on a level with the bottom juncture of stem and body of the retort. A 100 cc.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912

² *Chem. Ztg.*, **30**, 265-7 (1906).

³ *Chemische Revue ueber die Fett- und Harz-Industrie*, **14**, 112-3 (1907).

⁴ *Analyst*, **33**, 2-11 (1908).

⁵ *This Journal*, **2**, No. 5 (1910).

⁶ U. S. Dept. Agric., Circular **167**.

⁷ *Ibid.*, **167**, 2.

sample was taken and Table I shows the results obtained. It will be understood that volume percentages are referred to throughout this paper unless otherwise noted.

TABLE I—DIMETHYL SULFATE TESTS ON DISTILLATES

Number of sample	Name of material	250–315° C.		315–350° C.		350–375° C.	
		Percentage distillate by volume	Percentage insoluble in $(\text{CH}_3)_2\text{SO}_4$	Percentage distillate by volume	Percentage insoluble in $(\text{CH}_3)_2\text{SO}_4$	Percentage distillate by volume	Percentage insoluble in $(\text{CH}_3)_2\text{SO}_4$
1	Oil asphalt						
	Penetration 3.6 mm.	2.2	no test	11.8	80.0	28.8	90.0
2	Oil asphalt						
	Penetration 17.0 mm.	3.7	no test	15.5	85.0	28.0	90.0
3	Oil asphalt						
	Penetration 15.2 mm.	3.2	no test	16.8	87.5	17.2	90.0
4	California oil asphalt						
	Penetration 7.3 mm.	13.0	85.0	32.5	82.5	7.0	75.0
5	Fluxed Bermudez asphalt						
	Penetration 12.2 mm.	4.0	no test	12.0	85.0	17.1	85.0
6	Residual petroleum						
	Specific viscosity						
	Engler 50° C.—65.1	0.6	no test	6.8	90.0	25.2	90.0

It will be noted that in every case, except No. 4, the dimethyl sulfate insoluble tends to be greater in the higher fractions. The 270–315° C. fractions are too small for making the dimethyl tests with one exception, which in a measure indicates that it would be impossible to detect their presence in such fractions from mixtures containing small amounts of petroleum or asphaltic compounds.

These materials were then mixed with a crude coke-oven tar whose characteristics were as follows:

TABLE II—TESTS ON CRUDE COKE OVEN TAR

General character.....	Thin fluid
Specific gravity.....	1.173
Soluble in CS_2	95.23%
Insoluble in CS_2 (free carbon).....	4.71%
Ash.....	0.06%

DISTILLATION

Fractions	Percentage by volume	Percentage by weight	Character of distillates	Insoluble in $(\text{CH}_3)_2\text{SO}_4$
Water	0.6	0.5	Cloudy	
Up to 110° C.	1.6	1.3	Clear	None
110–170° C.	0.8	0.6	Clear	None
170–270° C.	17.5	15.5	1/2 solid	None
270–315° C.	9.4	8.2	1/2 solid	None
315–350° C.	11.0	9.7	Solid	None
350–375° C.	9.7	8.4	Solid	None
Pitch (over 375° C.)	49.4	55.8	Hard, brittle, glossy	
	100.0	100.0		

The mixtures were made, unless otherwise stated, by adding the given percentage by weight of petroleum or asphaltic product to the weighed amount of tar. The materials when necessary were rendered fluid by heating before mixing and in no case was there any separation of oil apparent. Distillations were then made in the manner above referred to, and fractions were taken at 270° C., 315° C., 350° C., and 375° C. Four cc. of the distillate from each fraction were treated with 6 cc. of dimethyl sulfate in a 10 cc. cylinder graduated to 0.2 cc. The resulting supernatant layer of insoluble oil was read and calculated to its percentage of the volume of sample taken. The results are shown in the following tables.

TABLE III—TESTS ON DISTILLATES FROM 10% MIXTURE

No. of sample	Mixture	315–350° C. fraction		350–375° C. fraction	
		Percentage distillate	Percentage insoluble in $(\text{CH}_3)_2\text{SO}_4$	Percentage distillate	Percentage insoluble in $(\text{CH}_3)_2\text{SO}_4$
1	90% coke oven tar				
	10% oil asphalt No. 2	11.5	5.0	17.5	25.0
2	90% coke oven tar				
	10% fluxed Bermudez asphalt	12.0	5.0	13.2	12.5
3	90% coke oven tar				
	10% residual petroleum	11.6	10.0	13.0	22.5
4(a)	Refined tar preparation				
	Free carbon = 19.36%	14.0	15.0	12.2	18.0

(a) Said to contain 10% oil asphalt.

In these 10 per cent. mixtures an excellent indication of the presence of oil asphalt is shown by the dimethyl sulfate test even in the 315–350° C. fraction, but there was no trace of open-chain compounds in the 270–315° C. fraction. No evidence of an oil product could be found in the total distillate obtained by distilling to coke by Sommer's method.

On account of the ease with which 10 per cent. could be detected by testing separate fractions, the test was not carried out with all the materials.

TABLE IV—TESTS ON DISTILLATES FROM 5% MIXTURES

No. of sample	Mixture	315–350° C. fraction		350–375° C. fraction	
		Percentage distillate	Percentage insoluble in $(\text{CH}_3)_2\text{SO}_4$	Percentage distillate	Percentage insoluble in $(\text{CH}_3)_2\text{SO}_4$
1	95% coke oven tar				
	5% oil asphalt No. 1	9.2	None	9.4	7.5
2	95% coke oven tar				
	5% oil asphalt No. 2	15.5	None	9.7	12.5
3	95% coke oven tar				
	5% oil asphalt No. 3	11.0	2.5	10.2	12.5
4	95% coke oven tar				
	5% Calif. oil asphalt	9.6	None	10.8	10.0
5	95% coke oven tar				
	5% fluxed Bermudez asphalt	11.0	None	10.8	8.0
6	95% coke oven tar				
	5% residual petroleum	8.5	7.5	12.5	12.5

In these 5 per cent. mixtures, the asphaltic base can still be detected in fairly large percentage in the last fraction (350–375° C.), but in only two cases (No. 3 and No. 6) out of six was there present a dimethyl sulfate insoluble in a lower fraction (315–350° C.).

TABLE V—TESTS ON DISTILLATES FROM 3% MIXTURES

No. of sample	Mixture	350–375° C. fraction	
		Percentage distillate	Percentage insoluble in $(\text{CH}_3)_2\text{SO}_4$
1	97% coke oven tar		
	3% oil asphalt No. 1	9.7	5.0
2	97% coke oven tar		
	3% oil asphalt No. 2	8.9	5.0
3	97% coke oven tar		
	3% oil asphalt No. 3	8.7	4.0
4	97% coke oven tar		
	3% Calif. oil asphalt	7.8	2.5
5	97% coke oven tar		
	3% fluxed Bermudez asphalt	8.1	1.25
6	97% coke oven tar		
	3% residual petroleum	10.4	10.0

In the 350–375° C. fraction of the distillations of the 3 per cent. mixture, the insoluble residue ranges

from 10 per cent. to 1.25 per cent. so that the detection of even three per cent. of asphalt is made possible by the method of fractionation which has been employed in this work. The 315°C . to 350°C . fraction did not give the slightest trace of insoluble products.

CONCLUSION

While the above results do not give any absolute idea of either the amount or exact nature of the material which has been fluxed with the tar, the authors feel that the improvement which they have made upon former methods may still prove of value, until a more exact method shall be forthcoming.

Specifications for tar-oil or tar-asphalt mixtures will be useless without some method of checking up the material submitted under them. We now think it possible, however, by specifying the grade and character of both the tar and petroleum or asphalt product to be used, and then obtaining data on similar laboratory mixtures, that we can determine with reasonable certainty whether our specifications are being fulfilled. In order to more closely determine the character of the material which has been fluxed with a tar, a volatilization test in conjunction with the dimethyl sulfate test will no doubt prove of great importance, and we feel that some accumulated data on these two tests will place us in a much safer position for specifying and identifying bituminous mixtures which present such difficulty to the chemist.

U. S. OFFICE OF PUBLIC ROADS
WASHINGTON, D. C.

THE DETERMINATION OF OXYGEN IN METALLIC TUNGSTEN POWDER AND SOME NOTES ON THE DETERMINATION OF OXYGEN IN STEEL

By CHARLES MORRIS JOHNSON

Received January 22, 1913

It has been found a distinct advantage both in the manufacture and use of tungsten powders to know their oxygen content. In one of the laboratories

gen in steel; *i. e.*, the ignition of the substance in a stream of hydrogen, which method is credited to Ledebur.

The electrically heated furnace introduced by the author¹ in 1908 for the direct determination of carbon in iron, steel and alloys is utilized in the process which is described in detail in this paper.

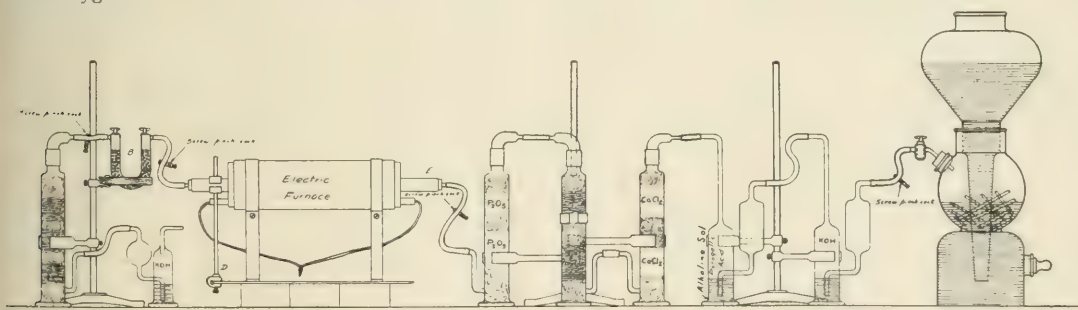
Walker and Patrick,² in a paper read at the Eighth International Congress of Applied Chemistry, attack the accuracy of the Ledebur method on the ground that any oxides of manganese or silicon present in the steel would not be reduced. The author regards the Ledebur method as more practical than the proposed new one³ above noted; even if the former process does not reveal the total oxygen present, it certainly shows enough of it to furnish a basis for judgment of the quality of the steel. If the steel is sufficiently dirty and poorly melted in actual open-hearth Bessemer or crucible practice to contain oxides of manganese and silicon, then it would surely contain enough oxide of iron to condemn it.

APPARATUS

The arrangement of apparatus is indicated in the drawing and the accompanying notes. The towers (or jars) are the author's design as are also J, I and C, and were first used as part of a combustion train.³ In this laboratory four furnaces are placed side by side. By the use of a Y tube at the outlet of jar F, one train from F to K can be made to serve two furnaces. Of course a separate set of A, B and C is necessary for each furnace. If, after making a large number of determinations, the blank begins to show a gradual increase, the contents of the various jars must be renewed.

METHOD

Blank.—Before introducing anything into the electric furnace, close all points marked "screw pinch cock." At B make a connection with a straight



APPARATUS

- A—Ignited asbestos and dry stick KOH.
B—Glass wool plugs and P_2O_5 (anhydrous powder)
C—Solution of KOH.
D—A clamp to prevent the quartz tube from moving since it was found that results varied if the tube moved back and forth.
E—Quartz tube.
F—Ignited asbestos and P_2O_5 , in alternate layers.
G—Ignited asbestos and dry stick KOH in alternate layers.

- H—Asbestos and small lump (size of pea) CaCl_2 in alternate layers.
I—50 cc. alkaline solution of pyrogallie acid.
J—50 cc. KOH solution.
K—Kipp generator 2 quart)

SOLUTIONS

- Potassium hydroxide 1 gram KOH to 1 cc. water.
Pyrogallie acid 3 grams pyrogallie acid and 2 cc. water to 3 cc. KOH solution
Kipp Generator Use stick zinc and dilute hydrochloric acid 1 : 1

under the author's direction, this determination is a matter of daily routine. The method involves the same principle used in the determination of oxy-

glass tube instead of the U tube shown. Insert

¹ J. Am. Chem. Soc., **30**, 773

² Proc. 8th Intern. Cong. Appl. Chem., **21**, 139; also THIS JOURNAL, **4**, 799.

³ J. Am. Chem. Soc., **25**, 862

quickly into the quartz tube at the point marked E) the porcelain boat that has been kept at 105°C in an air bath. Push the boat into the center of the furnace with a heavy copper wire which is marked to show how to place the boat in the hottest part of the furnace. Stopper the tube as quickly and tightly as possible. Open all four pinch cocks and turn on the hydrogen slowly until it passes through the apparatus at the rate of about seventy (70) bubbles per minute. Allow the hydrogen to pass through the cold furnace for thirty minutes. Close all the pinch cocks and replace the glass tube at B by the U tube. Open all cocks and let hydrogen run for another half hour to fill the weighing apparatus with this gas. Close all pinch cocks and the glass cocks on the U tube. Remove the U tube and weigh it quickly. Insert the U tube again, open all cocks and start the hydrogen flow; turn on the electric current in the furnace and bring up the temperature to $950\text{--}1000^{\circ}\text{C}$. After reaching this temperature keep the heat on for two hours with the hydrogen passing continually. Close all pinch cocks, shut off the hydrogen, and close the glass cocks on the weighing apparatus B. Detach and weigh B. The difference between this weight and the first weight represents the blank to be deducted from all determinations.

Sample.—Dry the finely ground powder of the tungsten metal to constant weight at 105°C . Put two or three grams of the powder into a porcelain boat that has been dried at 105°C . Place this in the cold furnace and stopper tightly at E. Using the glass connection at B, open the pinch cocks and allow hydrogen to pass through the cold furnace for one-half hour to remove whatever air entered when the charge was inserted. Close all pinch cocks and replace the glass tube by the weighed U tube at B. Open all cocks, adjust the hydrogen flow to 70 bubbles per minute and turn on the electric current, heating the furnace to $950\text{--}1000^{\circ}\text{C}$. Maintain this temperature for two hours with the hydrogen passing. Close all cocks and turn off the hydrogen. Remove and weigh the U tube. The increase in weight minus the blank gives the amount of water formed by the reduction of the metallic oxides to metal. This result multiplied by 16 and divided by 18.016 is equivalent to the weight of oxygen which is converted into percentage by the usual calculations.

STANDARDIZATION OF APPARATUS

WITH C. P. TUNGSTIC OXIDE.—This material is prepared as follows: Treat five grams of 96–98 per cent. tungsten powder in a platinum dish with 10 cc. c. p. hydrofluoric acid. Pour on this mixture very slowly 30 cc. of concentrated nitric acid. This produces considerable heat, and the material is dissolved as clear as water. Now add 15 cc. of concentrated sulfuric acid, evaporate to thick fumes, cool, add 10 to 20 cc. c. p. hydrochloric acid, boil three to four minutes, add 50 cc. of water, heat, filter, and wash free from iron and sulfates by decantation in a 600 cc. beaker. Transfer to a platinum dish, ignite at a bright red heat in a muffle, and put in a glass-stoppered bottle. Before using any of this material for a test, ignite a portion

of it at a blast-lamp temperature. Immediately after the blasting put one gram of the oxide in a porcelain boat dried at 105°C , and charge it at once into the furnace. It will require at least six hours treatment at $950\text{--}1000^{\circ}\text{C}$. to reduce this amount of oxide and carry all of the water formed over into the weighing apparatus.

WITH FERRIC OXIDE.—Dissolve 10 grams of low-carbon steel of very low phosphorus, sulfur and silicon content in 100 cc. hydrochloric acid in a liter beaker. Transfer this to a No. 7 porcelain dish and evaporate to 10 cc. Add 100 cc. nitric acid and evaporate to 20 cc. Add 50 cc. of concentrated nitric acid, and evaporate to dryness. Place the dish in a muffle and heat to redness. Cool, dissolve in 50 cc. hydrochloric acid, add 50 cc. of water; evaporate to small volume, filter out insoluble matter, such as silicic acid, and precipitate with filtered ammonia. Wash the precipitate by decantation until free from chlorides, dry in a porcelain dish, heat to redness, and place in a stoppered bottle. Blast a portion of this for three or four minutes, transfer 1 gram quickly to a porcelain boat, and place at once in the reduction furnace. Pass hydrogen for six hours after the furnace reaches $950\text{--}1000^{\circ}\text{C}$.

TABLE I—RESULTS OBTAINED BY APPARATUS DESCRIBED

Pure WO_3 , 20.69 per cent. oxygen
1 gram gave 20.70 per cent. oxygen
0.250 gram gave 20.80 per cent. oxygen
0.500 gram gave 20.30 per cent. oxygen
Average, 20.60 per cent. plus
Pure Fe_2O_3 , 30.05 per cent. oxygen
0.500 gram gave 30.16 per cent. oxygen
Blanks, 0.0030 and 0.0036

THE EFFECT OF FREE CARBON ON THE METHOD

It is an advantage to have some excess of free carbon in finished tungsten powder, and, at times, in the process of manufacture, it is necessary to know the amount of oxygen present in a powder that contains as much as three or four per cent. of charcoal. Some tests were made to see if the reaction $\text{WO}_3 + 3\text{C} = \text{W} + 3\text{CO}$ might not occur at the same time with the desired reaction $\text{WO}_3 + 6\text{H} = \text{W} + 3\text{H}_2\text{O}$. Table II shows that the presence of excessive amounts of free carbon caused no material error in the case of the pure tungsten oxide, but did cause low results when the carbon content exceeded five per cent. in the iron oxide. A curious feature is that thirty per cent. of free carbon caused practically no lower result than the addition of ten per cent.

TABLE II RESULTS OBTAINED WITH MIXTURES OF OXIDES AND CHARCOAL

Grams of mixture		Percentage Oxygen theoretical	Percentage Oxygen found	Percentage Carbon present
WO_3	Charcoal			
0.544	0.201	20.69	20.57	26.6
0.300	0.090	20.69	19.80	23.0
0.400	0.080	20.69	20.32	16.7
0.500	0.060	20.69	20.53	10.7
Fe_2O_3				
0.5785	0.000	30.05	29.84	None
0.473	0.208	30.05	27.35	30.5
0.400	0.122	30.05	28.68	23.3
0.300	0.089	30.05	27.53	23.0
0.500	0.025	30.05	29.95	4.7
0.500	0.050	30.05	27.82	9.7

The following table shows the amounts of oxygen found in the various brands of tungsten powders made both in the U. S. and abroad. Each numeral represents a different make.

The reduction was particularly poor in the second lot received from the German manufacturer designated as II (No. 2 in his second shipment). When so much oxide is present it can be easily detected by the eye, being equivalent to 10.92 per cent. of tungstic oxide. Such so-called metal has a distinct brown color.

TABLE III

Make	Imported or domestic	Oxygen found	Consignment
		Per cent.	
I	German	1.02	
II	German	1.10	No. 1
III	German	2.26	No. 2
IV	German	0.18	
V	German	0.53	
V	American	0.37	No. 1
V	American	0.47	No. 2
V	American	1.24	No. 3
VI	American	0.80	
VII	American	0.45	
VII	American	0.08	
VII	American	0.07	

THE DECARBONIZATION OF STEEL WHEN IGNITED IN A STREAM OF HYDROGEN FOR THE OXYGEN TEST

In 1909 the writer called attention to the fact that hydrogen will produce a bark, or decarbonized surface, on steels when the latter are heated in a current of this gas. Supplementing this statement¹ the following tests were made on three steels that were analyzed for oxygen:

TABLE IV

	Grams of drillings taken for the oxygen test	No. of hours ignited in hydrogen	Percentage carbon content	
			Before ignition	After ignition
Sample I....	9.6	3 ¹ / ₂	1.04	0.90
Sample II.....	16.0	3 ¹ / ₂	1.08	0.83
Sample III.....	19.5	3 ¹ / ₂	0.83	0.70

In the foregoing method, no preheating furnace or tube is used such as was recommended by Ledebur in his "Leitfaden für Eisenhütten-Laboratorien" and adopted by others who have since written on this or similar subjects, thus simplifying matters to that extent. Also, concentrated sulphuric acid is omitted, entirely, eliminating the possibility of unpleasant, not to say, dangerous accidents from this source.

The introduction of an alkaline solution of pyrogallol into the purifying train was made at the suggestion of Mr. Simon Lubousky, in July, 1912, when working under the author's direction. The latter adopted his suggestion as did Mr. McMillen,² of the Crescent Steel Works, who was the first to apply the electrically heated furnace, introduced by the writer, to the determination of oxygen.

LABORATORY OF THE PARK WORKS
CRUCIBLE STEEL CO. OF AMERICA
PITTSBURGH, PA.

¹ See "The Formation of White Scale on Steel and the Surface Decarbonization of Pipe-Annealed Steel," THIS JOURNAL, 1, 459 (1909).

² Met. and Chem. Eng., 11, No. 2; also THIS JOURNAL, Feb., 1913.

THE DETERMINATION OF PHOSPHORUS IN FERRO-TUNGSTEN, METALLIC TUNGSTEN POWDER, TUNGSTEN OXIDE AND TUNGSTIC ACID BY DIRECT SOLUTION

By C. M. JOHNSON

Received February 7, 1913

The author found in the course of an investigation that the practice of decomposing tungsten-bearing materials by fusing them with a mixture of sodium carbonate and potassium nitrate, leaching out the fusion, acidulating with hydrochloric acid, removing the tungstic acid by several evaporations to dryness, and then using the filtrate and washings from the tungstic acid for the determination of the phosphorus, gave far less of the latter element than was actually present. He then devised the following method which he has found to give near enough to the true phosphorus for technical purposes.

FERRO-TUNGSTEN.

Add 30 cc. of concentrated nitric acid to one gram of the powdered sample, in a platinum dish; then add slowly 3 cc. of C. P. hydrofluoric acid. Keep the dish covered with a watch glass; warm the mixture. After warming and slight boiling, the material should dissolve to a clear solution. Transfer the solution to a No. 5 porcelain dish and evaporate to dryness; do not bake as there is danger of losing phosphorus at this point. Dissolve this residue with 50 cc. of concentrated hydrochloric acid. Heat with the lid on; then remove the lid and evaporate to dryness; do not bake. Dissolve again, using 20 cc. of concentrated hydrochloric acid; heat, add 50 cc. of water, stir, heat and filter out the main tungsten; wash with one part of concentrated hydrochloric acid diluted with twenty parts of water. Evaporate the filtrate and washings to 10 cc., add 20 cc. of water, stir and filter as before. Evaporate to 10 cc., add 75 cc. of concentrated nitric acid and heat with the cover on until all action is over; remove the lid and evaporate to 10 cc. Add 50 cc. of nitric acid, and evaporate to 15 cc. Add 20 cc. of water, stir, heat and filter into a 6 oz. beaker; wash with two cc. of concentrated nitric acid diluted with 100 cc. of water, washing fifteen times. Evaporate the filtrate and washings in the beaker to 40 cc. Replace the lid and add a slight excess of five per cent. solution of potassium permanganate; boil three or four minutes. Dissolve the excess of manganese oxide with a little ferrous sulfate, and precipitate the phosphorus with molybdate solution.

When dissolving ferro-tungsten in the mixture of nitric and hydrofluoric acids, a porcelain dish can be used, but a little more hydrofluoric acid may be needed to secure complete solution of the alloy on account of the tendency of the latter acid to attack the dish. Further, when a porcelain dish is used, blanks must be run, using a standard steel. The latter is dissolved in the mixture of the two acids and the phosphorus determined, using the porcelain dish. If the standard is found to run higher than it should, the deduction necessary to correct it constitutes the blank to be subtracted from the phosphorus found in the sample.

Any method with which the writer is acquainted, using a carbonate and niter fusion of materials contain-

ing tungsten for the purpose of obtaining the percentage of phosphorus therein, gives only a fourth, or less, of the actual content of the latter element. The following results are only a few of those obtained in this laboratory and are given in proof of the above statement.

COMPARISONS OF FUSION AND EXTRACTION METHODS

Sample	Percentage author's extraction method	Phosphorus found by fusion with $\text{Na}_2\text{CO}_3 + \text{KNO}_3$
Ferro-tungsten No. 18.....	0.322	0.096
	0.350	0.088
	0.345	
	0.330	
A high phosphorus pig iron (0.73 per cent. P) - 0.5 gram tungsten powder (98 per cent. pure) per gram of iron.....	0.70	0.098
		0.095
"Tungsten cake".....	0.101	0.008
	0.102	
Tungsten powder oxidized to WO_3 at low red heat before extraction.....	0.113	0.007

TUNGSTEN ORES

Here the procedure differs only in the manner by which decomposition is effected. Grind the ore to the finest possible state of division; extract at nearly boiling temperature with 100 cc. concentrated hydrochloric acid in a No. 5 porcelain dish. About every thirty minutes, add 0.1 gram additions of KClO_3 ; on each addition of chlorate stir the sample off the bottom of the dish with a glass rod. Continue the heating, addition of chlorate and stirring until the tungsten ore has changed from a brown color to yellow in case of the dark ores; or from a light gray or brown to a very bright yellow in case of scheelite ore. Evaporate to dryness; cover, add 50 cc. concentrated HCl , heat 10 minutes to dissolve the iron and manganese, add 50 cc. of water and heat 15 minutes to allow the tungstic acid to separate well; cool and mix in some paper pulp. Filter through a double filter; wash with one part of hydrochloric acid diluted with twenty parts of water. Evaporate the filtrate and washings to 5 cc. and add 75 cc. of concentrated HNO_3 ; heat with the cover on the dish until all red fumes are gone and no further spraying occurs; remove the cover again and evaporate to 10 cc.; add 50 cc. of concentrated nitric and evaporate to 10 cc. again; dilute with 15 cc. of water and mix well. Filter into a 6 oz. beaker; wash with a one per cent. by volume solution of nitric acid, fifteen or twenty times. Evaporate the filtrate and washings to 40 cc. in the beaker; boil with a slight excess of permanganate solution. Add just enough ferrous sulphate to clear the excess of the hydrated oxide of manganese and boil again five minutes. Add 50 cc. of molybdate solution to the hot fluid in the beaker and finish the analysis as given for ferro-tungsten.

By careful heating and small additions of the chlorate, together with further applications of acid, if necessary, many dark ores can be so completely decomposed as to attain a clean orange color. The more complete the decomposition, the more perfect will be the extraction of the phosphorus. The hard black ferberites are the slowest to yield and take on the yellow color.

The decomposition can be done to the best advantage at a low-digesting heat and will require at least 5 or 6 hours.

This somewhat lengthy method is the only one that the author has found reliable, thus far, for technical purposes in tungsten ores. The latter may contain all the way from slight traces up to 0.500% phosphorus. The fusion method with these ores gives just as low results as with the ferro-tungsten. The cause of the low results is the formation of phosphotungstic acid; this is carried from the solution with the main tungstic acid that forms when the sodium tungstate is decomposed by acidulation and evaporation with acid.

METALLIC TUNGSTEN POWDER, TUNGSTIC OXIDE AND TUNGSTIC ACID

Ignite the tungsten powder at a red heat with frequent stirring until it is all converted to the yellow oxide. Then extract exactly as in tungsten ore for at least six hours and finish according to the ore method.

The original oxidation is best accomplished by weighing the sample into the dish in which the extraction is to be made and then placing dish and all in a muffle which is at a low red heat.

Tungstic acid and oxide do not require heating to redness. Their analysis for phosphorus is exactly like that for ores beginning with the hydrochloric acid-chlorate treatment.

Reserve the tungsten residues that are filtered out after the extractions and evaporations for the tungsten determination. The purification of these residues will be made the subject of a later publication.

NOTE.—It may be well in this article to caution those who have occasion to determine the phosphorus in molybdenum compounds, that any molybdic acid separating out of acid solutions containing phosphorus will carry a considerable amount of the latter element out, forming the analogous compound, phosphomolybdic acid.

LABORATORY OF THE PARKS WORKS
CRUCIBLE STEEL CO. OF AMERICA
PITTSBURGH, PA.

A COLORIMETRIC METHOD FOR THE DETERMINATION OF CHROMIUM IN STEEL

By FRANK GARRATT

Received January 6, 1913

A colorimetric method for the determination of chromium in steel, based on the use of Koenig's organic chromium reagent,¹ has been in use in the writer's laboratory for some time, and has given such satisfaction that it was deemed worthy of publication. The organic reagent used, disodium 1,8-dihydroxynaphthalene 3,6-disulfonate, is extremely sensitive to chromate solutions, and the method has been very useful for detecting chromium and determining what might be considered small percentages of this element.

The usual colorimetric methods for chromium have not found application for this determination in steel.

¹ *Chem. Ztg.*, **35**, 277 (1911).

Hillebrand¹ has made use of the color imparted to alkaline solutions by hexavalent chromium for the determination of this element in rocks. This method applied to steels, however, would require too large quantities of the metal to be handled conveniently for routine determinations, especially for small percentages, as the yellow color of the chromate does not lend itself to comparison so handily as the pink color obtained in the author's method. Moulin² has made use of the fact recorded by Cazeneuve that acetate of diphenylcarbazide gives a purple color with soluble chromates. The writer does not know of its being used for the determination of chromium in steel, however, nor could it be so conveniently applied as the colorimetric method described in this paper. The well-known qualitative test, making use of hydrogen peroxide and ether for the detection of chromic acid and chromates, is not capable of use, of course, as the blue color of the perchromic acid is not permanent.

The writer has occasion to make numerous determinations where the chromium runs 0.20 per cent. or under, and the results obtained by the method given below have been much more reliable than those obtained by other methods. The accurate determination of these small percentages of chromium is usually more troublesome than the larger quantities, but the new method takes care of these amounts very nicely. For determining the small quantities of chromium noted above, the writer has heretofore used McKenna's method³ and thinks it is uniformly more reliable than the other methods in vogue. The employment of concentrated nitric acid solutions and potassium chlorate is rather objectionable, however, and the method is not as convenient to handle as the colorimetric procedure described herewith. The color method is based on the fact that disodium 1,8-dihydroxynaphthalene 3,6-disulfonate gives pink to cherry-red colors when added to acid solutions of chromate salts. It is short and accurate, and as used in the writer's laboratory on routine work, is as follows:

From 0.2 to 0.4 gram of steel, depending on the amount of chromium present, is dissolved in 10 cc. of dilute sulfuric acid (1 : 3) in a 400 cc. Erlenmeyer flask. For steels containing 0.15 per cent. chromium or under the writer uses 0.4 gram of steel; for larger percentages than this 0.2 gram is sufficient to work on. When solution is complete, about $\frac{1}{2}$ cc. of concentrated nitric acid is added, and the solution boiled to near dryness to expel nitrous fumes and nitric acid. No more nitric acid is used than is necessary to oxidize the iron, as the presence of much free nitric acid interferes with the chromium color by giving it a brown tint. It is best to use a small marked tube that will deliver just about $\frac{1}{2}$ cc. for each determination. After driving off the nitric acid, 50 cc. of a 10 per cent. solution of sodium hydroxide are added, followed by the addition of about 1 gram of sodium peroxide, after which the solution is boiled for about five minutes. Since the reagent gives a

color with only chromate solutions, there should never be any free peroxide left in the flask, as the subsequent acidification would cause a reduction of the chromium compound to chromic sulfate. It has always been found, however, that five minutes boiling is sufficient to decompose the excess of peroxide. The solution is cooled to room temperature and diluted to 200 cc. in a volumetric flask; 100 cc. are filtered from this solution, and acidified by adding 2 cc. of 85 per cent. phosphoric acid, and 8 cc. of concentrated sulfuric acid. The concentrated sulfuric acid is purposely used to heat the solution, as the color, on the addition of the reagent, develops more quickly in a warm solution than in a cold one. The solution should not contain more than 20 per cent., by volume, of concentrated sulfuric acid, as stronger solutions than this seem to bleach the pink color. Immediately after the acidification, 2 cc. of a 1 per cent. aqueous solution of disodium 1,8-dihydroxynaphthalene 3,6-disulfonate are added. A pink to cherry-red color develops, depending on the amount of chromium present. The solution is allowed to stand for at least 15 minutes, and is then compared with a standard steel that has been treated in the same manner as the test.

The comparisons are usually made in a set of Camp's comparison tubes, although with very small percentages (say under 0.10) it is usual to use Nessler tubes. If a 0.20% standard is used it is diluted to 200 cc., so that each cubic centimeter represents 0.001 per cent. chromium. The writer prefers to use standard potassium bichromate solution added to a chromium-free steel as a source of standard, as the standard may then be varied to suit the composition of the steels being analyzed.

There is a very slight retention of some of the chromium by the iron precipitate. Experiments made along this line by taking samples through by the method described, and then comparing against pure solutions of potassium bichromate in sulfuric acid, indicated that about 95 per cent. of the true chromium value was obtained. The chromium recovery was very uniform, however, and since the standard is given the same treatment as the test the results should be accurate within practical limits. That this is true is shown by Table III.

The reagent gives a green color with ferric solutions, but this is instantly destroyed by adding phosphoric acid or strongly acidifying with sulfuric acid. The results have been found to be more reliable, however, in the absence of iron, and for this reason the precipitated ferric hydroxide is removed by filtration. Tungsten and molybdenum do not interfere with the determination of the chromium in any way whatever. The addition of phosphoric acid prevents the precipitation of tungstic acid, and thus gives clear solutions for comparison.

Vanadium interferes with the method, however, by imparting a brownish tint to the pink chromium color. Pure vanadate solutions give light yellow to amber-colored solutions, depending on the amount of vanadium present. When determining chromium

¹ *J. Am. Chem. Soc.*, **20**, 227 (1898).

² *Bull. Soc. Chim.*, **31**, 295 (1904).

³ *Chem. News*, **80**, 2, 67.

with moderate amounts of vanadium present the characteristic chromium color is but slightly changed, but the results are high as shown by Table I. The samples were compared against a 0.30 per cent. chromium standard that contained no vanadium.

TABLE I

Sample no.	Per cent vanadium present	Per cent chromium present	Per cent chromium obtained	Per cent error
1	0 10	0 20	0 23	+ 0 03
2	0 10	0 30	0 31	+ 0 01
3	0 15	0 30	0 35	+ 0 05
4	0 18	0 30	0 34	+ 0 04
5	0 20	0 30	0 37 (a)	+ 0 07

(a) Difficulty in comparing, owing to the solutions being of different shade.

The results in Table II also show the influence of vanadium on the determination of the chromium. The samples were compared against a 0.25 per cent. chromium standard that contained 0.15 per cent. vanadium. It will be noted that the samples containing more than 0.15 per cent vanadium were high, while those containing less than this amount were low

TABLE II

Sample no.	Per cent. vanadium present	Per cent chromium present	Per cent chromium obtained	Error
6	0 10	0 20	0 18	-0 02
7	0 10	0 20	0 18	-0 02
8	0 10	0 25	0 23	- 0 02
9	0 10	0 30	0 24	-0 06
10	0 20	0 20	0 22	+ 0 02
11	0 20	0 20	0 21	+ 0 01
12	0 20	0 25	0 28	+ 0 03
13	0 20	0 30	0 34	+ 0 04

The color due to vanadium is only obtained in acid solutions of the pentavalent compounds, and is quite characteristic. As a matter of fact, a few experiments made with pure vanadate solutions indicate that the reaction is quantitative, and is almost as sensitive as the well-known hydrogen peroxide test for this element.

The addition of the reagent to slightly acid solutions of quadrivalent titanium gives brick-red colors that are destroyed by adding hydrofluoric acid, or strongly acidifying with mineral acids. Concentrated sulfuric acid solutions of titanium, however, give pink colored solutions. The reaction for titanium is much more sensitive than the hydrogen peroxide test, but the percentage of free acid present has a very marked influence on the color, and it is not thought that a reliable quantitative method could be developed, owing to this fact. Titanium would not interfere with the chromium determination in the method as given, of course, as any titanium present would be precipitated and removed by filtration.

The writer does not think that the method given above is more advantageous for determining large percentages of chromium in steel (say over 0.60 per cent.) than Galbraith's or some such modification, but it seems to be particularly suited for small percentages of this element in steel.

Table III shows some results obtained by the new method.

The result on sample No. 14 was obtained by making an ether separation of the ferric chloride solution, and then replacing the hydrochloric acid with sul-

TABLE III

Sample no.	Weight of steel taken Grams	Per cent tungsten present	Per cent molybdenum present	Per cent chromium taken	Per cent chromium obtained	Error
14	2 0			0 012	0 013	+ 0 001
15	0 4			0 03	0 03	none
16	0 4			0 06	0 06	none
17	0 4			0 09	0 09	none
18	0 2			0 15	0 15	none
19	0 2			0 20	0 20	none
20	0 2			0 30	0 31	+ 0 01
21	0 2			0 50	0 49	- 0 01
22	0 2			0 70	0 70	none
23	0 2			1 10	1 10	none
24	0 2			1 40	1 38	- 0 02
25	0 4	5 5		0 20	0 20	none
26	0 4	5 5		0 30	0 29	- 0 01
27	0 4	20 0		0 20	0 20	none
28	0 4	20 0		0 25	0 24	- 0 01
29	0 4		5 0	0 20	0 18	- 0 02
30	0 4		5 0	0 30	0 29	- 0 01
31	0 4		10 0	0 20	0 18	- 0 02
32	0 4		10 0	0 25	0 25	none

furic acid. The chromium was then oxidized with sodium peroxide in an alkaline solution, and the small amount of ferric hydroxide removed by filtration. The solution of sodium chromate was then acidified with sulfuric acid, the chromium reagent added, and the color matched against a pure solution of potassium bichromate in sulfuric acid.

By taking larger quantities of steel, as in the case of sample No. 14, there is no difficulty in determining 0.001 per cent. chromium. Such a minute quantity of chromium in steel has no metallurgical significance whatever, of course, but the analyst is often called upon to look for very small quantities of metals, and it is a pleasure to have a method that will detect them without difficulty.

The writer is indebted to his assistant, Mr. D. J. Giles, for performing much of the experimental work leading up to the perfection of this method.

FIRTH-STERLING STEEL CO.
McKEESPORT, PA.

WATERS OF THE BREITENBUSH HOT SPRINGS, OREGON¹

By WALTON VAN WINKLE²

Received January 16, 1913

Breitenbush Hot Springs are near Breitenbush Creek on the west slope of the Cascade Mountains in Marion County, Oregon. Their exact elevation is unknown, but it is probably somewhat more than 2000 feet above sea level. The valley of the Breitenbush is narrow and the formations exposed are lavas of the Cascade Range series. Faults at the springs were not observed by Mr. Finkbiner, though possibly the waters issue from a fault. More than 60 hot springs, in three general groups, lie along both sides of the stream for almost a third of a mile. A few cold springs, entirely different in character, are within the limits of the groups, but as they are normal for the region they are unimportant. All the hot springs have nearly the same temperature and the manner of their grouping suggests a common origin. Reputed curative properties have been assigned to the various springs, and a crude "health resort" has been con-

¹ Published by permission of the director of the U. S. Geological Survey, dated January 4, 1913.

² Field work by N. M. Finkbiner

structed. Many patients take the waters each year, and if the place were more readily accessible it would undoubtedly enjoy a large patronage.

In September, 1912, Mr. N. M. Finkbinder, of the laboratory of the U. S. Geological Survey at Salem, Oregon, described 23 of the springs, and made field determinations of the temperature and alkalinity of each. He also collected from nine of these, from one cold spring, and from Breitenbush Creek above and below the springs, samples of water, which were analyzed conjointly at Salem by the writer, N. M. Finkbinder, and S. C. Dinsmore, state chemist of Nevada. The accompanying table gives results of both field and laboratory tests of these samples; the other 14 springs, field tests of which were made but are not reported, furnish water of similar character.

ANALYSES OF THE WATERS OF BREITENBUSH HOT SPRINGS, OREGON
(Parts per million unless otherwise designated)

	A	B	C	D	E	F	G	H	I	J	K	L
SiO ₂	141	134	142	138	144	141	151	147	142	142	24	24
Fe.....	0 85	0 10	0 17	0 20	0 10	0 10	0 80	0 10	0 05	0 27	0 70	0 01
Ca.....	99	93	89	90	86	95	93	97	90	93	5 2	4 4
Mg.....	1 7	1 5	1 2	1 5	1 5	1 5	1 0	0 8		1 4	2 4	1 1
Na.....	735				733					739		
K.....	41				41					41	8 7	6 9
CO ₂	0 0	0 0	0 0	0 0	0 0	0 0	0 0	0 0		0 0	0 0	0 0
HCO ₃	154	116	128	127	128	141	128	146		133	27	24
SO ₄	143	137	138	137	137	135	130	137	133	137	1 2	2 3
Cl.....	1,138	1,128	1,135	1,120	1,133	1,115	1,143	1,145	1,120	1,131	2 3	2 0
NO ₃	tr.				tr					tr	0 26	tr
Total dissolved solids at 180°.....	2,470	2,380	2,408	2,379	2,423	2,384	2,433	2,434	2,396	2,412	67	54
Temperature, degrees C.	67	59	73	73 5	73	69	69	83	66	70	13	

All samples collected Sept. 27, 1912.

A. Spring near right bank of creek at NE end of group. Flows from crevice in rock. Flow about "size of wrist."

B. "Arsenic spring" (no arsenic present) near left bank of creek about 600 feet SW from A. Flow one-half that of A.

C. Spring 43 feet from B and 84° NE of A. Flow same as A.

D. Spring 58 feet from B at 87° NE. Flows same as A.

E. Spring about 150 feet from B and due west. Flow one-fourth size of wrist.

F. Spring 175 feet from E and about 95° NW

G. Spring about 150 feet from F and 64° NW.

H. Spring at SW end of group.

I. Spring in main bath house. Difficult of access.

J. Average of analyses A to I inclusive.

K. Cold "Iron" spring on right bank of creek 250 feet above mouth of Mangfield Creek.

L. Composite sample from Breitenbush River.

The figures show that the several hot springs are merely separate outflows from a common source. The water is sodic chloride in character, but it contains small amounts of silica, calcium, bicarbonates, and sulfates. Minimum medicinal doses of both sulfates and carbonates might be obtained by drinking about 4 liters of the water,¹ but the disagreeable and even nauseating taste of the chlorides would make the drinking of that amount in one day an Herculean feat. It is certain that any curative properties attributable to the mineral content are psychologic rather than physiologic.

The water is interesting to geologists, as it is an excellent example of a type encountered in many regions of recent volcanic activity. Hot springs in volcanic regions may be placed in several general divisions, such as sulfate springs, carbon dioxide, or "soda" springs, chloride springs, and the like. The origin of the waters of many of the types can easily be explained, but no adequate explanation of the presence of the large quantities of sodium chloride in the waters of the third type has yet been advanced, so far as known to the writer.

The lavas of the Cascade Range have been erupted

¹ Cf. R. B. Dole, "Concentration of Mineral Water in Relation to Therapeutic Activity," in *Mineral Resources of the United States for 1911*. U. S. Geol. Survey, 1912.

or through these rocks would be heated, the bicarbonates in them would thereby be decomposed, and the waters would be relieved of part of their charge of iron, aluminum, alkaline earths, and carbonates. Alkaline salts with perhaps a slight residuum of calcium, and even less magnesium, would remain in solution. The calcic carbonate and the magnesia deposited would remain behind in the rock, and the water would move on without them. The carbonic acid set free as gas would react with rock silicates, decomposing them and depositing alkaline earth carbonates, the alkalies and part of the silica entering into solution. Thus a large part of the carbonic acid would be lost from the solution. The waters, percolating still further into the heated zone, would become further heated, and would be subjected to

through, and now overlies, the older sedimentaries of the continental floor. At the great depth to which the sediments have been buried, the adjoining lava is still hot. This heat has also been communicated to some extent to the sediments so that these are at high temperatures. As any waters, percolating into increasingly great pressures. They would become more strongly concentrated, because of these and other physical conditions, and would finally be forced to the surface under combined static and thermal pressure. Any carbon dioxide still held in solution would cause small amounts of calcium, encountered en route, to be dissolved, and the springs would then deliver a sodic chloride, calcic bicarbonated and sulfated water, containing appreciable amounts of dissolved silica. This explanation avoids the necessity of considering the action of magmatic, or "juvenile" waters, and, being based entirely on well-known chemical reactions, has the merit of simplicity, and freedom from speculative hypotheses.

U. S. GEOLOGICAL SURVEY
SALEM, OREGON

PHOSPHATES IN SURFACE WATERS

By GEORGE S. JAMIESON

Received February 5, 1914

The well-known colorimetric-molybdate method

is not suitable for the estimation of phosphates in the majority of surface waters because it is only applicable to those free from color.¹ In order to apply the method to the analysis of soil extracts, Veitch² removed the color from the solutions by evaporating them to dryness with magnesium nitrate and igniting the residues until the organic matter was burned. In the colorimetric method of Schreiner and Brown,³ which is based upon the precipitation of the phosphoric acid as ammonium magnesium phosphate, any color present is removed when the precipitate is filtered and washed with ammonium hydroxide.

Recently it has been found that the coloring matter of a water can be destroyed by heating the residue, obtained by evaporation, with potassium permanganate and nitric acid. In order to test the accuracy of the method, known amounts of sodium phosphate were added to 50 cc. portions of a surface water which had a light brown color. Each solution was acidified with 2 cc. of nitric acid (sp. gr. 1.07) and evaporated to dryness in porcelain dishes on the steam bath. The residue was moistened with 2 cc. of the diluted nitric acid and 0.5 cc. of a solution of potassium permanganate (1 gram per liter) was added. In the case of a highly colored water more permanganate should be added to insure complete decolorization. The solution was evaporated to dryness and the residue heated for an hour at 100° C., then the residue was heated with 3 cc. of the same nitric acid and 15 cc. of silica-free distilled water. The evaporating dish was given a circular motion to facilitate the extraction of the phosphoric acid from the insoluble matter. After standing a short time the solution was transferred to a 50 cc. Nessler tube and the dish was washed several times with small quantities of distilled water. When it is necessary to filter the solutions, the filters should be tested, as it has been pointed out by several investigators that sometimes even the best quality of washed filters may contain enough silica to contribute considerable color when the ammonium molybdate is added. It was found that thorough washing of the filter paper with hot water removed the silica. The solutions in the Nessler tubes were diluted to the mark with silica-free distilled water, and 4 cc. of ammonium molybdate solution which contained 15 grams of the neutral salt per liter were added. The color was developed and compared with freshly prepared standard tubes. The following results were obtained:

No.	Cc. of water	Mg. of P_2O_5 added	Mg. of P_2O_5 found
1	50	...	0.025
2	50	...	0.025
3	50	0.050	0.075
4	50	0.050	0.075
5	50	0.040	0.065
6	50	0.100	0.126

Two experiments were made using potassium chlorate in place of potassium permanganate with the modification that several evaporations were made with nitric acid in order to remove the larger part of the chlorides

formed by the reduction of the chlorate. This method gave 0.025 milligram of P_2O_5 in duplicate, using 50 cc. portions of the water for analysis. The potassium permanganate is preferred not only on account of its rapidity as compared with the chlorate method, but also from the fact, which has been previously shown,⁴ that low results are liable to be obtained with the latter method on account of the formation of *aqua regia* during the evaporations with nitric acid.

Phosphate determinations were made at various times upon several surface waters in the vicinity of New Haven, and it was observed that after a heavy or prolonged rain the amount of phosphate was considerably increased over the normal amount. It was further observed that the larger part of the phosphate was held in suspension as it could be removed by filtration. Three of the waters examined showed the normal amount of P_2O_5 to be about 0.6 milligram per liter. The average of 30 determinations (abnormally high results after rains being excluded) made upon different samples of water from a pond was 0.59 milligram of P_2O_5 per liter. In the following table, the results of several analyses are given of samples which were taken a day or two after heavy rains.

Water	Mg. of P_2O_5 per liter	Mg. of P_2O_5 per liter in filtered water
1 A	2.02	..
2 A	1.05	0.30
3 A	1.25	0.20
4 A	1.35	0.80
5 A	1.60	..
1 B	1.35	..
2 B	0.94	0.71
1 C	1.05	0.56
1 D	1.35	..
2 D	0.84	0.56

It is believed that the larger part of the phosphates introduced into these waters by the rains was due in part to the cultivated fields and in part to the inhabited areas upon the water sheds. This investigation indicates that the determination of phosphates in surface waters may be of assistance in showing pollution, and it is hoped that others more favorably situated may be able to investigate this problem thoroughly.

SHEFFIELD CHEMICAL LABORATORY
YALE UNIVERSITY, NEW HAVEN, CONN.

THE DETERMINATION OF ZINC IN ORES

By D. J. DEMOREST

Received October 14, 1912

The following modification of Low's method has been worked out in order that it may be applicable to any ore, no matter what impurities may be present. It depends upon the fact that ammonium carbonate completely separates zinc from iron, aluminum, manganese, lead and cadmium. The zinc (and copper) stay in solution as the zinc ammonia and copper ammonia carbonates. The copper is separated by hydrogen sulfide and the zinc is titrated by the well-known ferrocyanide method.

The writer's experience coincides with that of Low, that neither lead nor aluminum are safe reagents to

¹ A. G. Woodman and L. L. Cayvan, *J. Am. Chem. Soc.*, **23**, 96 (1901).

² *Ibid.*, **25**, 169 (1903).

³ *Ibid.*, **26**, 1463 (1904); also U. S. Dept. Agric., *Bur. of Soils, Bull.* **31** (1906).

⁴ A. G. Woodman and L. L. Cayvan, *J. Am. Chem. Soc.*, **23**, 96 (1903).

use to remove the copper and cadmium, as both lead and aluminum interfere in the titration of the zinc unless Waring's method is used.

Zinc usually occurs in ores as sulfide, oxide, carbonate or hydrosilicate. These minerals are dissolved by boiling strong mineral acids. Ores containing zinc spinel (Gahnite) must be fused with sodium carbonate and borax glass in order to be made soluble.

PROCESS OF ANALYSIS

Place one gram of the ore in a 250 cc. beaker, add 5 cc. of HCl (sp. gr. 1.2), heat for several minutes, add 20 cc. of concentrated HNO_3 and boil with the cover on until all brown fumes are expelled. Remove the beaker from the heat and add one gram of KClO_3 , and then boil to dryness. Do not bake the residue. Now add 50 cc. of hot water and one-half gram of KOH, but not more, and break up the cake on the bottom of the beaker with a policeman. Add 6 grams of ammonium carbonate and heat nearly to boiling for several minutes. Let the precipitate settle and filter, preferably by suction. Wash several times with a hot 5 per cent. solution of ammonium carbonate, then transfer the precipitate back to the beaker by washing it out of the funnel by a jet of water.

Dissolve the precipitate by means of 3 cc. of concentrated HCl and a little KNO_3 to reduce the MnO_2 present, add KOH solution until the acid is all neutralized, but no more, and then add 5 grams of ammonium carbonate and heat to boiling for several minutes. Filter through the same paper as was used before and wash several times with the hot 5 per cent. ammonium carbonate solution.

Make the filtrate, which should not be more than 200 cc., acid with HCl and then add 20 cc. more of strong HCl, keeping the cover on to prevent loss due to effervescence. Heat to 70° and pass a stream of hydrogen sulfide through the solution for several minutes. When the copper is practically all precipitated add, slowly and with stirring, 20 cc. of 1 : 1 ammonia and continue the stream of hydrogen sulfide for several minutes. Again heat to 70° and titrate. The volume at the beginning of the titration should be 250 cc. Fifty cc. of this should be reserved until the other $\frac{4}{5}$ is titrated roughly and then the 50 cc. added and the titration finished without consuming much time as the approximate amount of ferrocyanide required is known. The titration must be performed slowly and with constant stirring to get the best results.

STANDARDIZATION OF THE FERROCYANIDE

Dissolve 22 grams of pure $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ in water and dilute to one liter. One cc. of this solution will precipitate approximately 0.005 gram of zinc.

Weigh 0.2 gram of pure zinc, or better, the weight of zinc which is approximately equal to the weight of zinc in the sample to be analyzed. Dissolve in 10 cc. HCl and 20 cc. of water, add 10 grams of NH_4Cl , dilute to 250 cc., heat to 70° and titrate. Run the ferrocyanide in slowly and with constant stirring until a drop of the solution shows a brown tinge when tested

on a white plate with a drop of a 5 per cent. solution of uranyl nitrate. The color should appear within a minute.

A blank must be run, using the same amount of reagents and solution as is used in the standardization. It is necessary that the standardization be made under the same conditions of temperature, acidity, volume and rate of titration as obtained when the ore is titrated.

NOTES ON THE PROCESS

Potassium hydroxide is used to combine with any NO_3 ions present in order to prevent the formation of ammonium nitrate upon the addition of ammonium carbonate, because cadmium carbonate is soluble if much ammonium salts other than the carbonate are present.

The ammonium carbonate precipitates the lead, cadmium and any manganese present in solution as carbonates, the iron and aluminum precipitate as hydroxide; of course any lime or magnesia present comes down as carbonate. If the amounts of the elements which precipitate are small, one separation is sufficient, but it is always best to make a double separation. The second precipitation requires only a few minutes.

When the copper is precipitated according to the above directions, that is, by hydrogen sulfide from a very acid solution, the copper sulfide comes down free from zinc. What little copper remains in solution is precipitated as the solution is gradually made less acid. The copper sulfide need not be filtered off, for it precipitates in a very dense form and does not interfere with the end point, even when 20 per cent. of copper is present.

Potassium chlorate used in the decomposition of the ore introduces no complications, for the presence of hydrogen sulfide during titration prevents oxidation of the ferrocyanide. The zinc ferrocyanide always comes down white. It is absolutely necessary that the titration should not be made too rapidly. If the ferrocyanide is run in rapidly and without much stirring the end point will seem to be reached long before the zinc is all precipitated. If, however, the solution be then allowed to stand for several minutes while being vigorously stirred, titration may be finished correctly. Probably when the ferrocyanide is added rapidly, zinc potassium ferrocyanide is precipitated which can react with uranyl nitrate, giving a brown color.

The following are some results obtained by this method:

ZINC	PERCENTAGES OF METALS PRESENT			PERCENTAGE ZINC FOUND
	CADMIUM	LEAD	COPPER	
Sample D				31.37
Sample D	3.6			31.42
Sample D	3.6	10.5		31.30
Sample D.	3.6		10.0	31.35
Sample D	6.0	10.0	12.0	31.45

Sample D is the standard zinc ore of the U. S. Bureau of Standards, which the Bureau finds to contain 31.41 per cent. zinc.

GRAMS OF METALS PRESENT					GRAMS ZINC FOUND
ZINC	LEAD	COPPER	IRON	MANGANESE	
0.4175	0.21	0.10	0.15	0.08	0.4175
0.3425	0.12	0.06	0.10	0.05	0.3408

DEPARTMENT OF METALLURGY
OHIO STATE UNIVERSITY
COLUMBUS

A POLARIMETRIC METHOD FOR THE DETERMINATION OF STARCH IN PAPER

By CHRISTIAN E. G. POIST AND HARRY A. CROWN

Received January 7, 1913

The work described in this paper is supplementary to that given in a paper under the same title, which was submitted to the Eighth International Congress of Applied Chemistry, but too late for publication, and also to the authors' paper, "Research on Lintner's Polarimetric Method for the Determination of Starch," which was published among the original communications to the Congress.

In our previous work, we found that the method could be applied to the determination of starch in paper with reliable results. But it was found necessary to determine the value of the specific rotatory power for small amounts of starch, as this value varies from that found and given in our paper on Lintner's method, depending on the amount of starch taken in work. Therefore, the object of the present work was to determine the specific rotatory power of starch for low concentrations, similar to those encountered when working with 5 grams of paper and to test the method more fully on a large number of samples of paper.

When weights of starch below one gram were taken, the value for $[\alpha]_D^{20}$ varied considerably, duplicates not checking well. This discrepancy seemed due to the precipitation of some of the starch by the phosphotungstic acid. Its use was then omitted as it is not necessary to precipitate the protein which is low in the pure starch and does not affect the reading. But when the phosphotungstic acid was not used, the starch solutions obtained were cloudy, due to the small amount of fat which is present in the starch, and the polarimetric readings could not be made with sufficient accuracy.

It was then decided to add some paper pulp to the starch solution, this producing the same conditions as when samples of paper which give clear solutions are worked upon. The result was satisfactory, the pulp absorbing the fat and giving a perfectly clear filtrate. Pure Swedish paper pulp was used and the solutions obtained were clear, even when as much as five grams of starch were dissolved. Blank tests

Weight of starch taken Grams	Reading in 200 mm. tube Degrees Ventzke	$[\alpha]_D^{20}$ Degrees
0.1	0.6	207.0
0.2	1.2	207.0
0.3	1.8	207.0
0.4	2.4	207.0
0.5	3.0	207.0
0.6	3.6	207.0
0.7	4.2	207.0
0.8	4.8	207.0
0.9	5.35	205.1
1.0	5.9	203.6
1.5	8.85	203.5
2.0	11.8	203.5
3.0	17.5	201.5
4.0	23.2	200.1
5.0	28.9	199.4

were run on the paper pulp which was found to be free from starch.

Working with pure corn starch, the preceding values for the specific rotatory power were obtained.

The method by which these values were obtained is as follows:

The pure starch of known weight is mixed with 20 cc. of distilled water in a mortar, which is cooled in ice-water. To this is added 40 cc. concentrated HCl previously cooled down in a freezing mixture, stirring with the pestle until all the starch is dissolved, and then the solution is kept at 20° C. for half an hour. The contents of the mortar are then transferred to a 200 cc. flask to which had been added about one gram of pure paper pulp, disintegrated by rubbing in a mortar with HCl of 1.125 specific gravity, and the flask is filled to the mark at 20° C. with HCl of 1.125 specific gravity. The flask is kept for half an hour in a water bath at 20° C. and then the solution is filtered, first with suction through a Büchner funnel, the paper pulp acting as a filtering medium and then through a Munktell washed filter. Just fifteen minutes after the first filtration is begun, the reading is taken at 20° C. in a 200 mm. tube.

About sixty samples of paper were now tested by the above method, for starch retained, the addition of paper pulp being omitted, but the other details followed as above. The value 207.0 for $[\alpha]_D^{20}$ was used in all computations since the maximum reading obtained was 1.5° V. In all the samples tested, the percentage of starch retained varied from 0 to as high as 4.7 per cent. Two or three samples contained coloring matter which imparted a dark red color to the HCl solution, making it impossible to obtain a polarimetric reading. Some papers gave yellow solutions but this color did not affect the readings. Results in duplicate checked well and on the whole, the method worked satisfactorily.

CORN PRODUCTS REFINING CO.
EDGEWATER, N. J.

LABORATORY AND PLANT

CHEMICAL ENGINEERING AND THE NEW LABORATORIES AT COLUMBIA UNIVERSITY¹

By M. C. WHITAKER AND R. K. MURPHY

The development of the manufacturing industries

¹ Paper presented at the New York Section of the American Chemical Society, Chemists' Club, New York, March 7, 1913.

produces an ever-increasing demand for men trained in the fundamental sciences and their applications. Manufacturing processes based upon chemical principles are advancing in importance at a most astounding rate. To supply properly trained men who can

develop, operate and direct these manufacturing processes would seem to be one of the most important present-day problems in technical education. Most institutions have not met the problem fairly; they have hesitated, procrastinated and even evaded. The problem is not one which can be solved by grafting extra instruction here and there on to some existing engineering courses nor by changing the name of the chemist to that of chemical engineer.

The new industrial development calls for a new class of men—men trained to apply engineering methods and appliances to the solution of chemical problems and the operation of chemical processes.

The training of chemical engineers has been given the most careful study by Columbia University.

are no longer able to adequately prepare young men to complete a thorough scientific course in four years without an undue strain upon the student.

There are but two possible methods of solving the difficulty: (1) a reduction in the amount of material presented, or (2) an arbitrary increase in the time to be devoted to post-high school training. In many schools the academic subjects are being eliminated from the curriculum to the great loss of the students' general scholarship; in other institutions fundamentals are superficialized to such an extent that the graduate lacks the necessary foundation on which to develop; in still other engineering courses, cultural and fundamental subjects are retained and engineering applications neglected. In the few cases where the faculty

TENTATIVE PLAN OF A THREE-YEAR COURSE OFFERED BY COLUMBIA COLLEGE TO FULFILL THE REQUIREMENTS FOR ENTRANCE TO THE POST GRADUATE ENGINEERING SCHOOLS

FIRST YEAR

<i>First Half</i>		<i>Second Half</i>	
SUBJECT	POINTS	SUBJECT	POINTS
Advanced Algebra (Math. 1).....	3	Analytical Geometry (Math. 4).....	3
English Composition (Eng. A).....	3	Chemistry, Gen'l (2 Lect.) (Chem. 3, 6 lab.).....	5
Principles of Science (Philosophy A).....	3	English Composition (Eng. A).....	3
Modern Language based on Intermediate Entr. requirement.....	5	Principles of Science (Philosophy A).....	3
Shop Work (1 aft.).....	1	Modern Language (continued).....	3
Physical Education A.....	1	Shop Work (1 aft.).....	1
		Physical Education A.....	1
		Total points.....	35

SECOND YEAR

<i>First Half</i>		<i>Second Half</i>	
SUBJECT	POINTS	SUBJECT	POINTS
Calculus (Math. 15).....	4	Calculus (Math. 16).....	4
Gen'l (2 Lect.) (Chem. 4c) (6 lab.).....	5	Chemistry (Chem. 67) (2 Lect.) Qualitative (6 lab.).....	5
Introduction to Eng. Lit. (English B 3).....	3	Physics (3 Lect., 3 Rec.).....	6
Epochs of History (Hist. A).....	3	Epochs of History (Hist. A).....	3
Drafting (2 afternoons).....	2	Drafting (2 afternoons).....	2
Geometry, Descriptive (Drafting 3).....	3	Total points.....	40

THIRD YEAR

<i>First Half</i>		<i>Second Half</i>	
SUBJECT	POINTS	SUBJECT	POINTS
Calculus (Math. 17).....	4	Physics (same).....	7½
Chemistry (Chem. 68) (2 Lect.) Qualitative (6 lab.).....	5	Statics (Mechanics 2).....	2
Physics (3 Lect., 3 Rec.) (1 afternoon Lab.).....	7½	Political Science (Politics 4).....	3
Political Science (Econ. 1).....	3	Surveying (Civil Eng. 2).....	2
		Mineralogy (2 Lect.) (1 afternoon).....	3
		Total points.....	37

ELECTIVES

The 12 additional points necessary to establish the 124 points required for the degree of B.S. must be made either by extra credit for high standing by work in Summer Sessions, or by free election during the second and third years; such electives may be chosen at the student's option from among the courses in which he can satisfy the prerequisites, with the single provision that no program aggregating more than 22½ points will be approved for any half year.

Prominent men have been freely consulted, and the entire problem has been attacked on its broadest and most comprehensive basis. It is felt that a distinct advance has been made, and it is the purpose of this paper to present a brief outline of present plans and progress.

It is a recognized fact that the rapid advancement in all engineering sciences has put a heavy burden on the student. The time allotted to cover the work (usually four years) has remained constant, while the ground to be covered has been greatly increased. The High Schools have endeavored to keep pace with the more severe requirements of the technical school entrance examinations, but these preparatory schools seem also to have reached their limit. They

is about evenly divided between academic and engineering representatives, the student's wail concerning the amount of time at his disposal for study and his difficulty in assimilating the various and varied subjects offered in the distended curriculum, has been drowned by the insistent appeals of the faculty members for more allotted time for each of the so-called "most important subjects" in the course. The obvious remedy to meet this deplorable situation is to give the student more time and better facilities in order to fulfill the present demands.

The Schools of Mines, Engineering and Chemistry of Columbia University will become, in 1914, regular post-graduate professional schools and will require a college degree or its equivalent for admission. The

purpose of these changes is not only to provide better and broader undergraduate training for students of engineering, but also to place the engineering departments upon the same high professional plane as that occupied by the departments of law and medicine. It is a significant fact that for several years over twenty per cent. of the students in our engineering schools were college graduates, and therefore really post-graduate students.

The college training taken as a preliminary preparation for this new post-graduate course in engineering must necessarily include physics, chemistry and fundamental mathematics, in addition to the usual college courses. In a properly arranged curriculum this

years in the time to be devoted to the combined fundamental and professional work will not only relieve the present tension on instructors and students, but will produce a class of graduates immeasurably better qualified to assume the responsibilities of their profession.

Chemical Engineering courses must eventually teach men to use engineering methods and engineering appliances in solving chemical problems and carrying on chemical processes. These engineering appliances and methods are not to be found in the test tube, beaker, or funnel of the usual chemical laboratory any more than steam, hydraulic and electric appliances and applications are to be found in

NEW THREE-YEAR POST-GRADUATE COURSE IN CHEMICAL ENGINEERING

FIRST YEAR

<i>First Half</i>			<i>Second Half</i>		
SUBJECT	LECT.	AFT.	SUBJECT	LECT.	AFT.
Physical Laboratory.....	0	1	Advanced Heat.....	3	0
Mechanics.....	3	0	Mechanics.....	3	0
Industrial Chemistry.....	3	0	Industrial Chemistry.....	3	0
Power Machinery.....	2	0	Power Machinery.....	2	0
Physical Chemistry.....	3	1	Physical Chemistry.....	3	1
Elements of Electrical Engineering.....	2	0	Electrical Machinery.....	2	0
Hydraulics—Theory.....	2	0	Hydraulics—Laboratory.....	0	1
Quantitative Analysis.....	2	3	Quantitative and Engineering Chemistry.....	2	3
	—	—		—	—
Total.....	17	5	Total.....	18	5

SUMMER WORK

Chemical Factory Inspection (2 weeks)
Factory work with detailed report on some assigned industry (6 weeks)

SECOND YEAR

<i>First Half</i>			<i>Second Half</i>		
SUBJECT	LECT.	AFT.	SUBJECT	LECT.	AFT.
Organic Chemistry.....	3	2	Organic Chemistry.....	3	2
Machine Elements.....	2	0	Machine Elements.....	2	0
Food and Sanitary Chemistry.....	3	0	Adv. Industrial Chemistry.....	3	0
Engineering Thermodynamics.....	3	0	Engineering Thermodynamics.....	5	0
Direct Current Laboratory.....	1	1	Alternating Current Lab.....	1	1
Resistance of Materials.....	5	2	Assaying.....	2	2
	—	—		—	—
Total.....	17	5	Total.....	16	5

SUMMER WORK

Chemical and Mechanical Engineering Laboratory (8 weeks)

THIRD YEAR

<i>First Half</i>			<i>Second Half</i>		
SUBJECT	LECT.	AFT.	SUBJECT	LECT.	AFT.
Introduction to Metallurgy and Metallurgy of Copper.....	3	0	Metallurgy—Lead, Zinc, Gold and Silver.....	3	0
Metallurgy—Iron and Steel.....	1	0	Chemical Factory Management.....	3	0
Chemical Factory Machinery.....	3	0	Steam Power.....	4	2
Electrochemistry.....	2	1	Business Law.....	2	0
Gas Power.....	2	1	Chemical Engineering Lab. Special Problems.....	0	3
Commercial Organic Analysis.....	2	3	Seminar.....	6	0
Seminar.....	5	0		—	—
	—	—		—	—
Total.....	18	5	Total.....	18	5

ground may be covered in three years. A tentative scheme, planned by the Faculty of Columbia College to meet the requirements for admission to the new post-graduate engineering schools, is given on page 305. The subjects offered in this undergraduate course are now to be found in the schedules of practically all colleges, and by judicious elections the required fundamentals may be satisfactorily completed in any good institution.

Corresponding courses have been adopted for Mining, Mechanical, Electrical and Civil Engineering. It is believed that this extension of practically two

a physics laboratory. Mechanical and electrical engineers long ago recognized the difference between the equipment needed for studying the application of the fundamental scientific principles to complicated engineering conditions, and the equipment necessary to study the laws and principles upon which these fundamentals are based. Laboratories, equipped with mechanical and electrical engineering appliances, have long been established to meet these needs, but the corresponding chemical engineering laboratories have been sadly lacking.

The chemist, with characteristic conservatism pro-

duced by many disappointments, has been slow to recognize the point at which the study of principles ends and the study of application begins. He has hesitated to develop laboratories with commercial apparatus, such as pumps, siphons, tanks, filter presses, evaporators, stills, centrifugals, absorption towers, etc., but has preferred to consider his work completed with the establishment of a principle on a test-tube scale. It is at this point that the Chemical Engineer is needed to take chemical principles and engineer them in the same manner as the mechanical engineer engineers the physics of heat and the electrical engineer engineers the physics of electricity. The chemical engineer has but little chance to successfully engineer chemical operations unless he knows the fundamental methods and appliances available. The chem-

we shall have a laboratory of, chemical engineering comparable with the best laboratories in mechanical and electrical engineering.

Some photographs serve to show the plan and scope of our work and the progress thus far made. The division of space is shown in Fig. 1, from which it will be noted that we have, besides the large general laboratory, the electrochemical laboratories, paper and textile laboratory, four research laboratories, grinder room, pipe shop, machine shop, furnace room, etc. Some of the more typical equipment now installed and in operation is illustrated in Figs. II-VI. The solution and precipitation tanks, the filter presses, the siphons and stirrers are partially illustrated in Fig. II.

The problems assigned in all operations have been

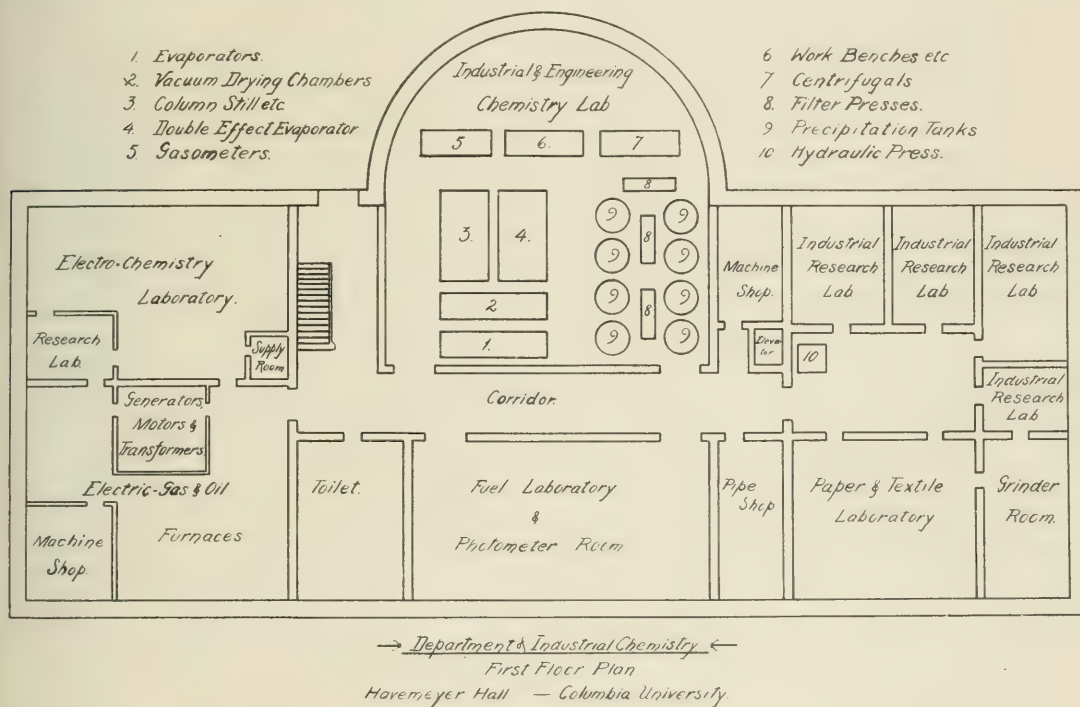


FIG 1

ist cannot establish data with a beaker and test-tube on which to engineer a process any more than a mechanical engineer can arrive at a correct conclusion in regard to the performance of a steam boiler by some experiments with a tomato can.

Besides the new industrial laboratories which occupy the entire lower floors of the Havemeyer building, there are the new Nichols laboratories for general chemistry and the new physical chemistry laboratories which are nearing completion. Only the former will be described.

THE NEW CHEMICAL ENGINEERING LABORATORIES

The accommodations for the industrial laboratories are by no means ideal, but while the scheme is not yet complete, we have made a bold beginning and hope to expand rapidly from year to year. Ultimately

selected so as to be cyclic as far as possible with the object of reducing operating expenses to a minimum and also avoiding the accumulation of products. For example, in the work involving the use of tanks, acid siphons, pumps, filter presses, etc., a squad of four or five students, with one acting as foreman for a complete operation, is given the problem of dissolving a weighed quantity of the waste sulfates of the didymium earths in dilute sulfuric acid in a lead-lined tank, with air agitation. The solution is transferred by means of a lead siphon to another tank and precipitated as oxalates, which settle readily; the liquid is returned to the acid tank for future use, the precipitate washed by decantation, filter-pressed, and the press cake vacuum-dried and weighed. The cake is then transferred to a seamless wrought-iron tank

and converted to hydroxides using a steam air agitator. The oxalate solution is stored for use in the evaporator and the hydroxides after filter-pressing are dissolved in acids and returned to the first tank. During this operation the student has had experience with solution, precipitation, washing by decantation, filtration of a granular crystalline precipitate, conversion from a solid insoluble in acid to one soluble, filtration of a slime and resolution in acid; air, steam and mechanical agitation; pumps, lubricators, siphons, etc. All this work is done on a quantitative basis;

or double effect. The student squad on this operation, after becoming perfectly familiar with the vacuum pumps, the condenser, the sampler and the various valves and connections, makes an efficiency run by evaporating water, first as single, and then as double effect. The capacity and distribution of heat are determined by thermometer and pressure gauges, weighing the steam used, the water evaporated from each pan, the condenser water, etc. The next step is to concentrate a salt solution containing some six to eight hundred pounds of common salt. Here the



FIG. II. FILTER PRESSES, PUMPS, SIPHONS, TANKS, AGITATORS, ETC.

the losses are checked and must be accounted for at each stage.

The vacuum-drying apparatus is illustrated in Fig. III; it is used in several of the operations, such as drying press-cakes and solids obtained from evaporation, etc.

The double-effect evaporator, shown in Fig. IV, has some special features. The main connections are fitted with outside screw and yoke gate valves so that it is possible to tell at a glance which valves are open and which are closed. The connections are also arranged to permit the pans to be run as either single

solubility curves must be studied and plotted, the original solution analyzed and the maximum amount of salt obtainable calculated. The squad is then given the problem of separating two salts of different solubilities. For example, several hundred gallons of a mixed sodium oxalate and sodium chloride solution are worked; this requires careful study of the solubility curves, frequent sampling and hydrometer readings, and some skill in operation due to foaming and other difficulties which must be met and overcome. The efficiency tests with one and then two salts in solution are compared with the runs on

water alone, and the relationship of the inches of vacuum in each pan and the effect of varying either of the vacuum pumps or initial steam pressure carefully studied. The final product is weighed, then vacuum-dried to get the dry basis, and finally transferred to the proper tanks and redissolved for use by the next squad.

A part of the distillation equipment is shown in Fig. V. The bench of ten steam-jacket evaporators and the pot stills are not shown, but a fairly good idea of the copper column still with condensers and ex-

method of procedure without being told just how to perform each step.

Another view of the laboratory is illustrated in Fig. VI, showing a centrifugal dryer, centrifugal clarifier and filter, Blau-gas welding outfit and some of the gas holders.

The dyeing laboratory is equipped with the necessary apparatus including an experimental calico printing machine, to demonstrate the applications of the different classes of dyestuffs and mordants for dyeing various fabrics such as cotton, wool, silk and

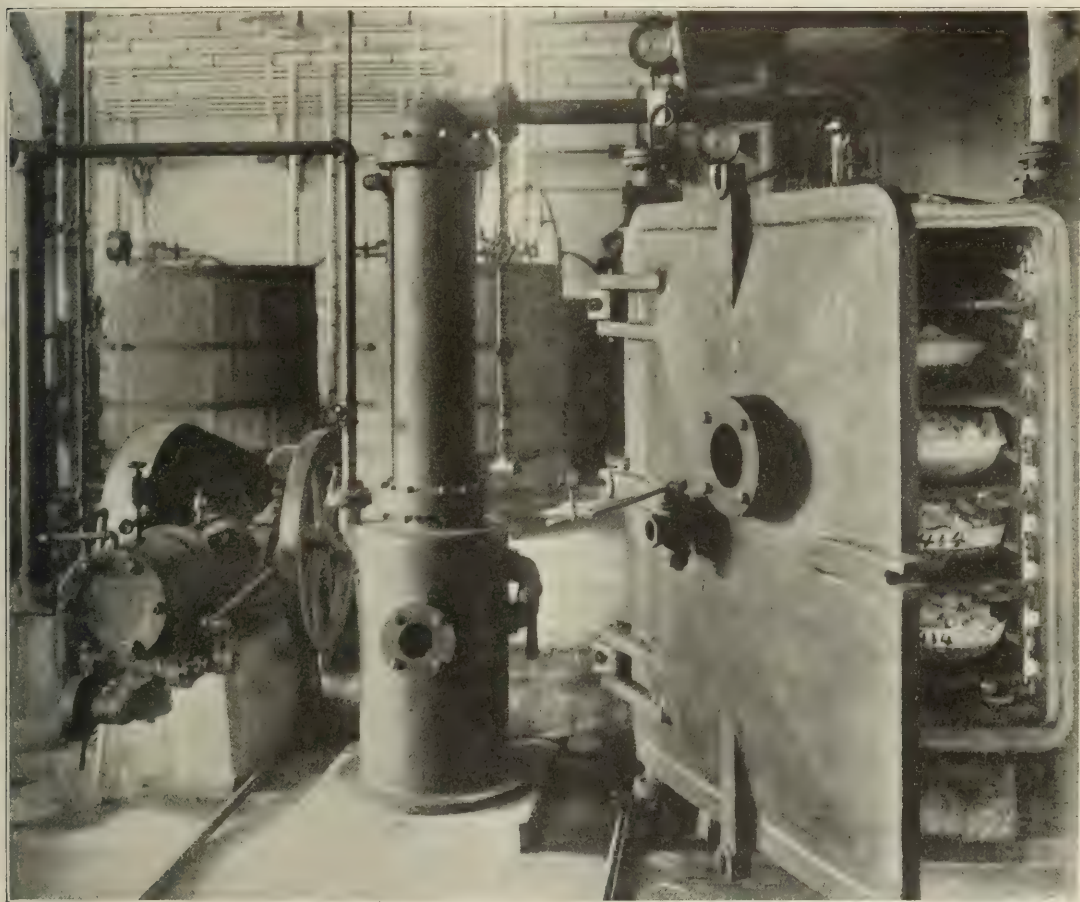


FIG. III—VACUUM SHELF DRYER, CONDENSER AND PUMP. 42 INCH SHELVES

tractor may be gained from the illustration. The problems to be solved here are similar to the ones already described in some detail. After thoroughly standardizing the apparatus and operating on water alone, this squad would be given the problem of making 98 per cent. pure acetone from a 50 per cent. solution containing some mud or other solid which must first be removed in a pot still before purifying in the column still. Another problem given is to make fifty pounds of soda crystals. The squad must look up the chemistry involved and determine on the

artificial silk. The laboratory course includes such work as is necessary to familiarize the student with the application, testing and matching of dyestuffs, determinations of fastness, etc. In connection with the dye work, instruction is given in the use of the microscope and ultra-microscope for the identification of fibers, crystals, starches, yeasts, etc., and such other testing methods as would be of value to the chemist or chemical engineer in commercial operations.

A new paper laboratory has been started and at present is equipped with an iron soda digester (2 gal.

capacity), a bronze sulfite digester (7 gal. capacity), pulp beater, rotary copper drum dryers and mechanical stirrers. Fig. VII illustrates the soda digester with stirring device. A 110 lb. steam line runs into the laboratory and this may be connected to the various digesters, etc. Several men are doing research work on the treatment of woods and on paper sizing.

Instruction in the electrochemical branch of industrial chemistry is given in the senior year of the Chemical Engineering course. The laboratory work includes not only all the usual electrolytic processes, but also considerable practice with various types of electric furnaces. Electric power from the central

calculations. The problems arising as a result of transferring operations from the laboratory to the large scale factory appliance may here be met and solved under the sympathetic eye and patient hand of the developer, instead of being doomed to failure by being delivered in incomplete form to unsympathetic and busy works managers. One of the industrial research laboratories is illustrated in Fig. IX and needs no further explanation beyond that it contains all the ordinary equipment such as gas, electricity, blast, suction, water, drying ovens, etc.

Students are given the greatest possible liberty in the methods of handling their problems, and are allowed to make mistakes and get experience. They

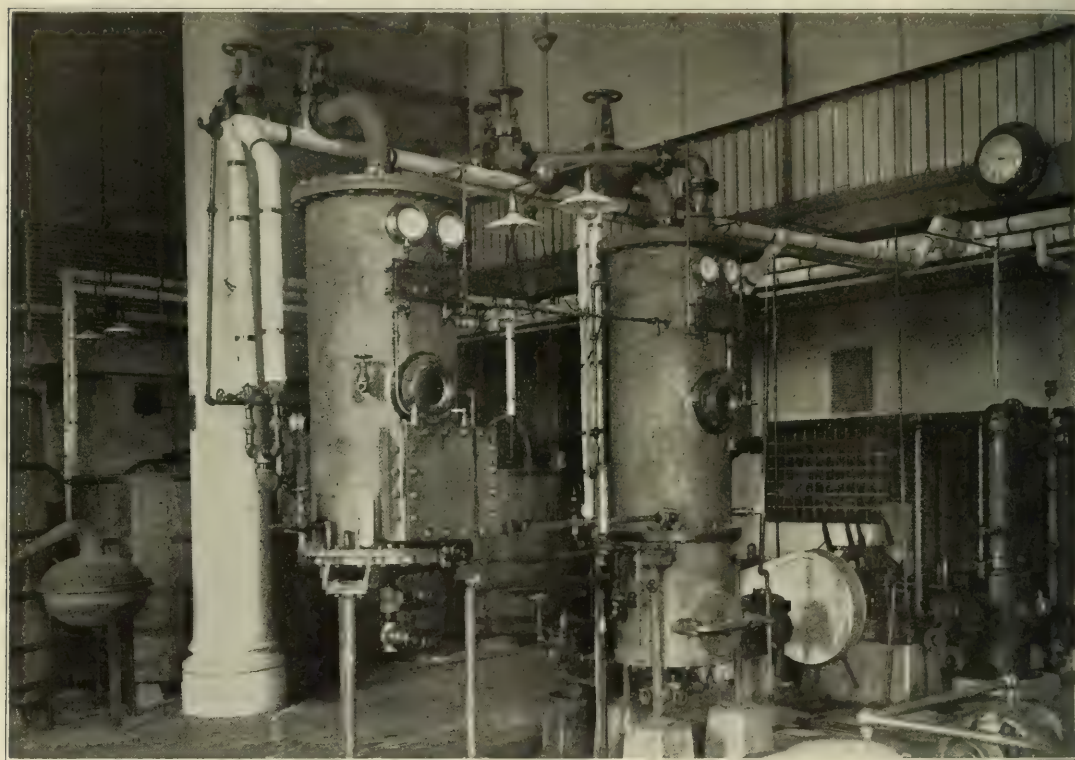


FIG. IV—DOUBLE-EFFECT VACUUM PANS (24 IN.) WITH COMPLETE EQUIPMENT—CONDENSER, VACUUM PUMP, CIRCULATING PUMP, SALTING-OUT CHAMBER, ETC.

power plant is transformed in the dynamo room to almost any desired amperage and voltage. A part of the dynamo room is shown in Fig. VIII. This view gives an idea of the direct current dynamo set and the power available for experimental work.

Facilities for individual research work are very good, and many students avail themselves of the opportunity to do advanced work beyond the required courses. Research men find standard equipment of modern and approved types ready and available for trying out any fundamental practice on a scale and in a way which will enable them to establish data capable of being used on a practical basis and in business

use apparatus as types of equipment already developed to carry out the devised operations. Soon they become familiar with the limitations of the appliances and learn to exercise engineering judgment in overcoming their difficulties. A preliminary report covering the chemistry involved and the general method of procedure is required of the foreman of each group, but each member of the squad must hand in a final detailed report covering all points of the work performed. It is the duty of the instructors to assign problems and supervise processes, but not to assist or tabloidize the work for the students.

In conclusion, it should be pointed out that neither

the course as outlined nor the laboratory as planned is in any sense intended to train men as artisans or skilled operators. The students are not taught how to dye cotton or silk or to print calico, but are in-

and engineering methods involved in vacuum evaporation. Familiarity with the equipment of such a laboratory will give young men that facility of application which comes now only from long experience.

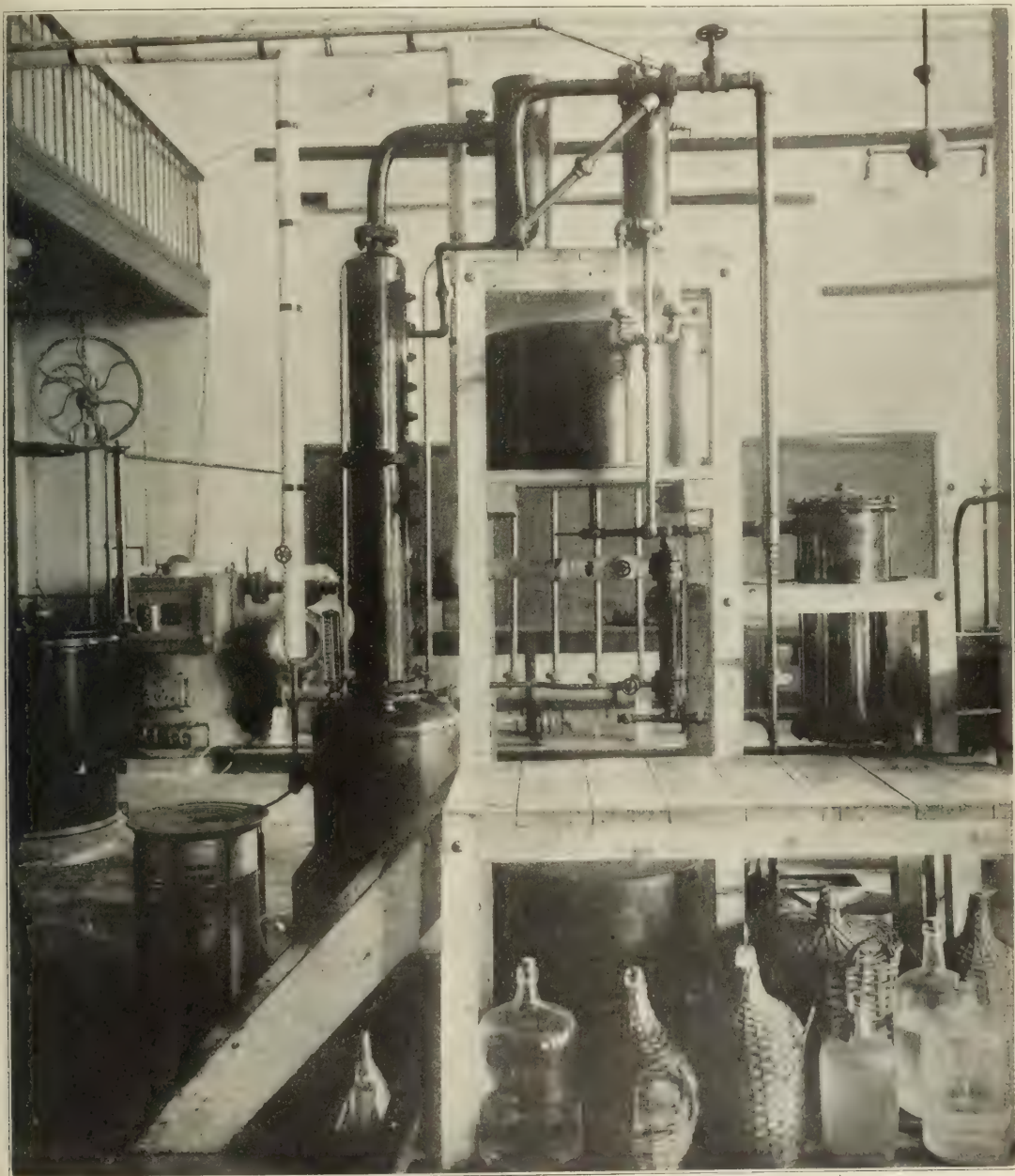


FIG. V. COLUMN STILL AND EXTRACTION APPARATUS. CAPACITY, 10 GALS. PER HOUR.

structed in the application of the fundamental chemistry and physics involved in this industry. We are not trying to teach men to run sugar pans but hope to give them a broad conception of the principles

The student develops that engineering instinct which is so essential to the successful solution of chemical engineering problems.

It is confidently believed that the new graduate

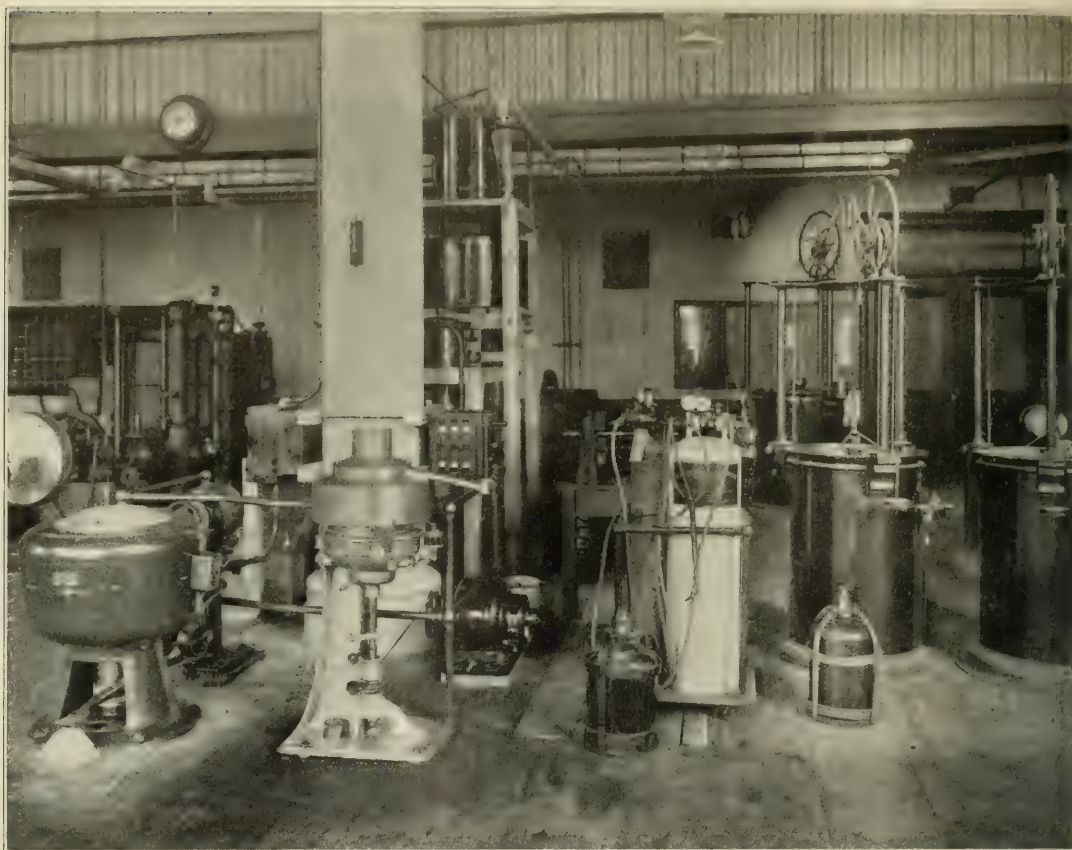


FIG. VI—GENERAL VIEW SHOWING WHIZZER, CLARIFIER AND FILTER, WELDING OUTFIT AND GAS HOLDERS

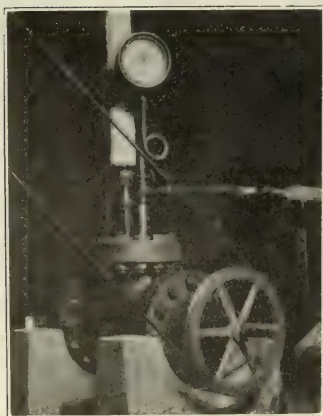


FIG. VII—SODA DIGESTER

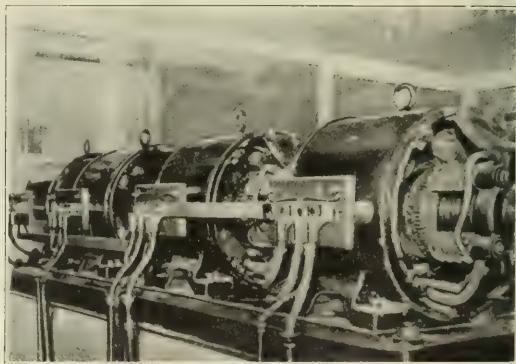


FIG. VIII—MOTOR-GENERATOR SET IN ELECTROCHEMICAL LABORATORY

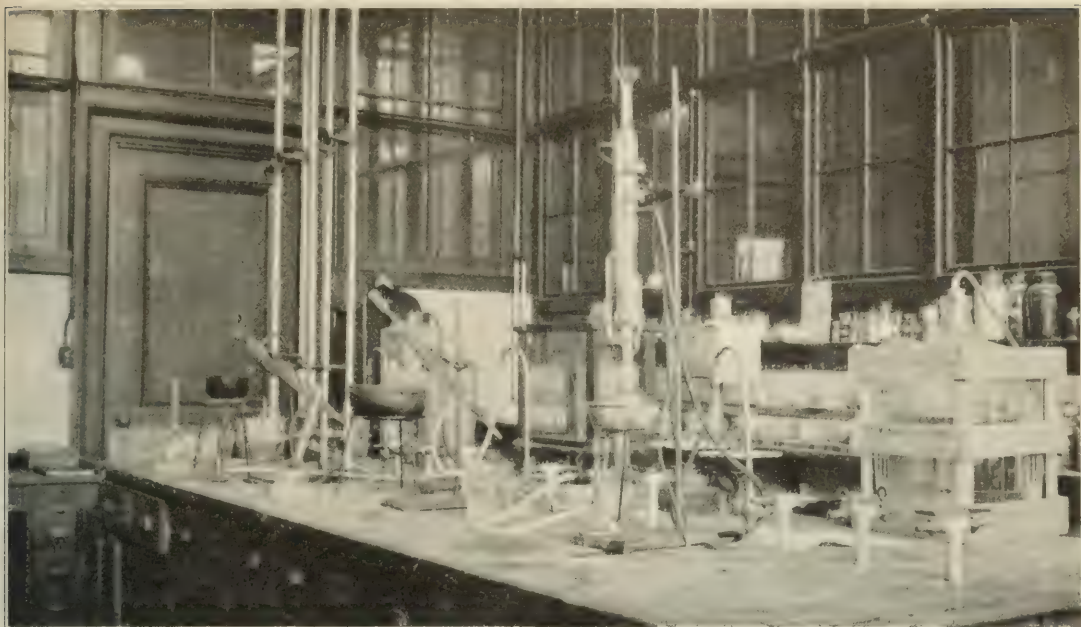


FIG. IX.—TYPICAL RESEARCH LABORATORY TO ACCOMMODATE TWO OR THREE POST GRADUATE STUDENTS

courses and instruction in Chemical Engineering at Columbia, based as they are on a good general fundamental education, will produce men capable of rapidly advancing to positions of responsibility in this most promising profession.

HAVEMEYER HALL, COLUMBIA UNIVERSITY
NEW YORK CITY

TECHNICAL ACCOUNTING AND CHEMICAL CONTROL IN SUGAR MANUFACTURE¹

By DAVID L. DAVOLL, JR.

(Concluded from the March issue)

THE CONTROL

SAMPLING AND ANALYSIS

THE CANE.—Determine fiber and sugar once each factory day.

Sampling.—Every hour, four representative canes are to be selected under the chemist's supervision, as they pass from cars, wagons or hopper to the first unit of the tandem. Reserve in a cool, shaded place. If

the factory runs six hours or less, prepare the whole sample; if more, subsample to 24 canes as follows: Sort into three piles, one containing the pieces bearing evidence of having been cut in the fields next to the root; one, pieces cut from the middle; one, pieces bearing base of the "cog-ollo" or top of the cane. Take, impartially, eight

pieces from each pile and cut into transverse slices $\frac{1}{8}$ — $\frac{1}{16}$ inch thick by means of a Pellet cane cutter, feeding the tops to the machine first and rejecting no odd ends. Allow the slices to fall into a galvanized iron box large enough to hold the entire sample; throw upon a large, clean piece of enameled cloth, mix well and quickly subsample by "coning and leveling" until about a liter is obtained; weigh this carefully. Chop in a hopper resting upon a clean piece of enameled cloth, with a heavy cane knife (calaboso) when finished. brush up all pieces that may have fallen upon the cloth and again weigh.

Correct for loss by drying out during chopping. The hopper must be employed for cane exclusively.

Sugar Determination.—Lightly pack 52 grams in a continuous extractor¹ and slowly pour through the mass sufficient 40 per cent. alcohol to fill the 4-oz. Adams' flask two-thirds full; maintain the flask contents faintly alkaline with basic lead acetate; extract for three-fourths hour or for such time as experience shows, under working conditions, is sufficient to extract the sugar to 0.05 per cent. limit using a perforated

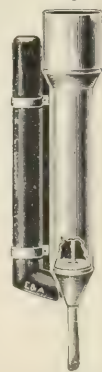


FIG. 2.—CONTINUOUS EXTRACTOR

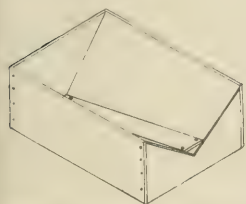


FIG. 1.—HOPPER FOR CHOPPING CANE

¹ Paper presented at the Fifth Annual Meeting of the American Institute of Chemical Engineers, Detroit, December, 1912

¹ NOTE.—This extractor is made of milled copper and is very durable. vapor pipe insulated, thus promoting rapid exhaustion of contents besides serving as a handle, it is suitable for use with cosettes, "pulp," drug and material of many kinds calling for restricted quantity of solvent.

Especially designed to eliminate "bumping" entirely. An easily removable, screen diaphragm retains the material in place, which, after extraction, may be quantitatively removed for drying and weighing. Made by Eimer & Amend, New York. Standard size 11 cubic inches net capacity.

asbestos plate and low flame, place the flask upon the water bath and expel the alcohol; rinse into a 100 cc. flask, add sufficient basic lead acetate, fill to the mark, filter and polarize. The reading divided by 2 equals sugar.

Fiber Determination.—Lightly pack 52 grams in the continuous extractor, allow cool or tepid water to run slowly through during 12 hours; then, slowly, about a liter of water heated to 60° C.; connect the flask containing 40 per cent. alcohol and extract for three-fourths hour; withdraw dregs by means of the rod attached to the bottom sieve diaphragm to a drying dish; dry for 2-4 hours to constant weight at

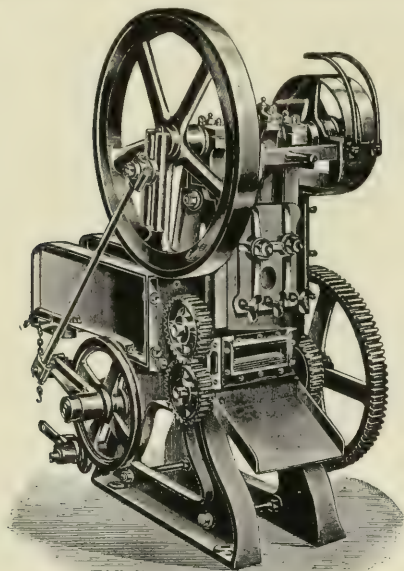


FIG. 3—BAGASSE CUTTING MACHINE

105-110° C. Calculate fiber. To dry cane or bagasse fiber, employ shallow, oblong, tin trays, 4" by 5" and 1 5/8" deep, bottom consisting of copper cloth of 80-100 meshes per linear inch.

THE BAGASSE.—Sugar may be determined every 2 hours, fiber once a factory day. Well ground bagasse (modern milling) may be taken by the handful as it rises from the mill-boot of the discharge conveyor and tightly pressed into the sample can, which may be 2 feet deep by 1 foot diameter. Fifteen minutes intermittent sampling should fill the can and there should be the minimum delay in preparation for analysis.

Coarse bagasse (such as that of the first, second or even third unit of the tandem on old-style milling) should be taken from its particular conveyor, *clear across* the blanket and amount to at least 1 1/2 cu. ft. in volume.

Throw the can contents to the floor upon a large sheet of enamelled cloth, tearing coarse pieces apart by hand. If still warm (hot saturation) cover lightly with a second sheet of cloth for a few moments.

Rapidly mix by stirring and rolling, exposing the minimum surface and pile in a cone; level from the apex outward to a truncated cone and withdraw a wedge-shaped sample in size proportionate to the coarseness of the bagasse. Cut up the whole sample and mix. A fully satisfactory machine for quickly reducing large amounts of bagasse to fine "sawdust" is that made by Boot and Krantz, The Hague, Holland. See Fig. 3.

Polarization. This is performed as under cane, with the alkalinity maintained with 5 per cent. solution Na_2CO_3 .

Fiber Determination.—This necessitates a very finely divided material. The Hawaiian Sugar Chemists' Association defines fiber as "the total insoluble solids," water being the solvent.

Quantitatively remove the residue left after extraction of the sugar to a drying tray and dry for about an hour, then transfer to a large, loosely covered container; do this on every sample of the factory day. At the close of the day there should be, in the container, the practically dry residues of 12 normal weights. Mix well, weigh the accumulated samples, take one-twelfth, place in a drying tray and dry for 2-3 hours or to constant weight. Divide the weight by 26, multiply by 100, and the result is percentage fiber in bagasse.

If 10 samples only have been extracted, take one-tenth, etc.

Alternate Sugar Method.—Use that as adopted by the Hawaiian Chemists' Association, 1910, *Bull.* 32, Agricultural and Chemical Series, Experiment Station, Hawaiian Sugar Planters' Association, by W. S. Norris.

Moisture.—This serves to judge of the tax laid upon the furnaces by reason of the water to be evaporated; calculate by "difference."

MILL RAW JUICE corresponds to the diffusion juice of the beet industry. It is the main basis of sugar accounting and great pains should be taken to make it fully representative of the work.

Sampling.—The following method by means of a thin, rapidly-running stream has been found to be representative.

Modern mills, in general, discharge the mill raw juice from the free end of a pipe into a small reserve or overflow tank, which in turn serves the measuring or weighing tanks proper.

At a point a short distance below the level of the discharge (in order to secure a slight "head") the main discharge pipe is tapped by a half-inch pipe in such a manner that a small quantity of juice continuously finds the way to its destination, the reserve tank, through it. A small copper wire, preferably not over 4 inches long, may now be attached to the end of the half-inch pipe and a thin stream of juice diverted so as to discharge through a hole in the side of a covered, 2-gallon pail. Another location for this half-inch pipe, not quite so advantageous, is in the same main raw juice line but close to the pump, returning the diverted portion of juice to the pump-tank and interposing the copper wire in the stream, as described. This latter arrangement reduces the pump efficiency

about 1 per cent. in a 1000-ton factory. The half-inch pipe should have but one cock, and that next the open end, to allow for closing when the pump is not operating.

The collection of samples is apt to be a weak point, on account of placing too much reliance upon a messenger. It should be reduced to a simple system, proper conveniences supplied, and closely supervised. In tropical work, evaporation is rapid and the air is full of spores. All samples should be removed from the factory at frequent intervals: let the chemist either analyze them at once or properly preserve them. The messenger may collect the following samples every two hours: mill raw juice, first mill juice, last mill juice, residual juice, evaporator thin juice and meladura. Assuming that these are already discharging into their containers there will be needed for substitution six other clean and dry sample pails containing sufficient formaline. Not all of the sample collected can be or should be taken to the laboratory—after mixing, the greater bulk will be at once returned to the process of manufacture. For this purpose, separate clean and dry metal paddles will be needed for stirring. A tray of light material holding six liter Mason jars, plainly labeled and with screw tops, will be needed for receiving the sub-samples.

Analysis.—Strain the sample into a clean, well-rinsed Mason jar and let stand until the foam has risen; carefully remove the same with a teaspoon. *A. The Brix:* Slowly fill a tall cylinder by pouring down the side; carefully insert the hydrometer, let stand until it has come to permanent rest, then read and note the temperature; correct for hydrometer error, if any and to standard temperature. *B. The Polarization:* Slowly fill a 100–110 cc. flask to lower mark, clearing up any uncertain meniscus with a drop of ether, run in the prescribed amount of basic lead acetate and fill to the upper mark with water; shake thoroughly, filter and polarize, employing the Schmitz table for sugar percentage. If the analyses must be made at longer intervals, composite as follows: Prepare as above for "A" and "B;" instead of proceeding with "A," pour 200 cc. into the compositing jar containing the proper amount of formaline, for Brix: proceed with "B" as far as filtration, then pour the whole contents of the flask into the compositing jar for polarization.

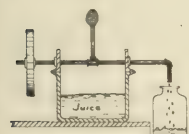


FIG. 4—JUICE SAMPLER

When making the determination, thoroughly mix the contents of each compositing jar, proceeding as under "A" for Brix. Filter, polarize and consult Schmitz's table for sugar percentage.

C. Set aside in a suitable jar a portion of the unfiltered "leaded" solution for the daily composite determination of sucrose by the Herzfeld-Clerget method and invert sugar.

When making these last two determinations, add sufficient acetic acid to transform all basic lead acetate into neutral or slightly acid condition, correcting for increased volume in final calculation.

FIRST MILL JUICE. Sampling.—This must be representative of juices coming from combined crusher and first unit of the tandem. There is no agreement in either Brix or sugar content nor in the quantity of the juices falling from (1) the crusher, (2) the cane roll, (3) the bagasse roll; hence the logical place for continuously and systematically drawing this sample is in the trough conveying it to the mill raw juice pump. Fig. 4 shows a successful device for taking this sample.¹

An objection to this will sometimes be that water used to cool the mill bearings finds its way into this sample, the effect being to raise the figure for extraction.

The trough sample then becomes useless and a second sample should be taken by placing a suitable pail beneath the cane roll of the first unit at a point where tests show that the Brix and sugar content correspond to those of the trough sample when not contaminated by water. This pail holds about 8 liters and has a cover slightly inclined; holes are made near its apex, from the inside outward, sufficient in number to about half fill the pail in 2 hours.

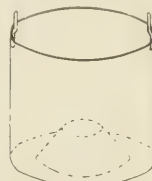


FIG. 5

Analyze as under mill raw juice, A and B only.

THIRD MILL JUICE.—The sample, where saturation is practiced, is taken from its pump discharge pipe as described under mill raw juice. Where it is not, the spoon sample may be used in the trough. For analysis, see under mill raw juice, A and B only.

RESIDUAL JUICE.—This is the drip from the bagasse roll of the last unit of the tandem and should be taken continuously, as under first mill juice and analyzed as under raw mill juice, A and B.

EVAPORATOR THICK JUICE.—The Brix of each tank filled should be taken. Where fluctuation in purity is considerable, as between 70 and 85 for instance, facilities should be at hand for rapid determination of purity. For this and similar work the author has introduced the Pellet continuous polarizing tube.

FILTER PRESS CAKE.—The loss from this source is seldom correctly determined. At reasonable intervals the laboratory messenger should go to the trucks located below the presses and as a press is dumped, break off small pieces from a dozen large cakes; if semi-fluid, a cup should be used. Analyze in the usual way but substitute 25 grams for a normal weight to allow for insoluble material. Periodically the weight of the press cakes should be determined.

THE SUGARS.—Large centrales employ fans for cooling and rendering the sugar more uniform. Where not used, the net weight per sack must be verified when cold and finally loaded. The weight is still held by custom at 325 Spanish pounds of 460 grams each.

Sampling.—A clean and dry galvanized iron box, of about 1 cu. ft. capacity and having a funnel-shaped hopper in the cover, is placed at the sugar scales, to be changed once in 6 hours.

¹ NOTE.—The "spoon" sampler consists of a large spoon having a hollow handle of copper communicating with a hollow shaft of small piping and discharging through an elbow into a pail charged with formaline. The shaft, driven from the mill-roll, should make about 8 revolutions per minute. The spoon is covered with fine screen to keep out "trash."

From every bag in five, and before adjusting the weight with sugar from the storage bin, the truckman will transfer a pinch of sugar from bag to sample box. As the sample is taken away, the serial number of bags filled will be recorded, in order to arrive at the number of bags represented, in proportion to which the polarization is to be adjusted in taking off averages.

Preparation.—The sugar is poured upon a plate of glass, all sticks and foreign matter removed and thoroughly mixed with a clean steel spatula. Lumps are reduced with a porcelain roller and incorporated with the rest of the sample. Polarize at once. Determine moisture once a day. Composite a small portion from each sample for the semi-monthly chemical statement upon which is to be determined: (1) polarization, (2) true sucrose, (3) dry substance, net, (4) invert sugar, (5) ash, (6) total dirt, (7) ash in total dirt.

When the sugar contains over 1 per cent. moisture, the sample for compositing is to be dried in a water-bath oven for a short time, later correcting the final analytical data back to the basis of the average of the daily polarizations upon the fresh sample.

Polarization.—A normal weight is placed in a funnel and washed into a 100 cc. flask with 50 cc. of water, completely dissolved by rotating, then clarified by basic lead acetate solution and 2 cc. of alumina cream. As a rule not over 1 cc. of lead solution is needed for high-grade centrifugal (96) sugars and from 2–6 cc. for molasses sugars (80–90). Use the minimum quantity necessary for clarification. After the lead and cream are in, allow air bubbles to rise and complete volume to 100 cc. Mix and filter in a carefully covered funnel, discarding the first runnings. Endeavor to polarize at the temperature of dilution.

THE MASSECUITE.—Applicable to either grained or blanc strikes.

Measuring.—Massecuite intended for the crystallizers should be measured after being placed therein, at the moment of entering and for every strike; the same applies to sugar wagons or tanks. The volume of material subject to crystallization in motion for long or short periods or "at rest" for many days, should be known as an important step in control.

An accurate account should be kept of the movement in and out, so that at any time, by consulting the records, a balance can be struck of the exact amount in stock.

Sampling.—Take a portion equal to 2 liters from at least three places as the mass is struck from the vacuum pans, *viz.*, after it is running well, in the middle of the flow and towards the end.

Analysis.—At the laboratory the following tests are made: (1) purity of the mother liquor, (2) Brix by double dilution, (3) polarization.

Purity of the Mother Liquor.—Grained massecuite only. Investigations upon the work of competent sugar boilers has shown that this test has a very important bearing upon economical boiling. The drop in purity may be very variable for equal purity of strike. Immediately after being drawn the sample is to be rapidly turbinated in the small laboratory centrifugal.

The author has devised special, light-weight, tin linings for the centrifugal; these can be kept on hand in any number, they slip in and out easily, collect the whole sample and do away with the necessity of cleaning the centrifugal. It is especially helpful in making a large number of such analyses.

When the lowering of purity is abnormal, either way, the several causes to which it may be due should be investigated. The purity is determined after diluting to 18–20° Brix.

Polarization.—This is made by taking either a normal or double-normal weight of the sample used for determining the Brix by double dilution, according to color, and proceeding as under the sugar polarization, excepting that after filtration the solution must be acidulated before reading, *viz.*: Fill a 50–55 cc. flask to the 50 cc. mark with the clear filtrate, add dilute acetic acid to faint acidity and complete to the 55 cc. mark with water; shake and polarize; increase the reading by one-tenth to compensate for the dilution.

When possible, clarify with neutral lead acetate and thus avoid later dilution.

EFFICIENCY OF CRYSTALLIZERS.—This refers also to work carried on "at rest" in tanks or wagons. The mother liquor is separated by the laboratory centrifugal and its purity determined at 18–20° Brix, when the product is about half discharged from the vessel.

FINAL MOLASSES.—This should invariably be weighed, being too viscid to measure and occluding much air.

Under a suitable arrangement one man can attend to the day's output. The well mixed day's composite sample is analyzed for Brix by double dilution, sugar and purity (calculated).

Daily a quantity in proportion to the amount made is set aside for the semi-monthly complete analysis, as detailed under sugar.

Control of the Boiling.—Much can be accomplished at the pan-service tanks to bring about regulated, economical boiling. If they are uniform in size, deep, rather than broad, large rather than small and with facilities for rapid and thorough cleaning, much will have been gained. The several molasses are diluted to an exact Brix, generally 60° and heated to 70° C. at a "blow-up" station over these tanks. Every tank and piece of apparatus in the factory should bear a number. These tanks should be graduated to 10 hectoliter units, vertically, upon a scale having an indicator actuated by a float.

Before the contents of a tank is started for feeding the vacuum pan the following data concerning the material is to be entered upon the sugar-boilers black-board: Date, hour, tank No., name of material, temperature, Brix, and where possible, the purity.

Upon the basis of this data the massecuite purity is established and the finished product should agree within two points of the estimated.

WEIGHTS AND MEASURES AS AFFECTING MILL EXTRACTION.—(1) The *Sugar Cane* is bought by the Spanish ton as a matter of tradition. From the time it enters the factory the metric system should apply.

It suffers variable shrinkage in weight before it is ground and proper chemical control has necessitated the present policy of weighing it upon a beam scale at the hoist just before discharging into the mill hopper.

(2) The *Mill Raw Juice* is generally measured and when properly carried out, this will furnish a basis of calculation for the amount of sugar introduced (the real object) quite as satisfactory as weighing. Foam and occluded air have been the cause of some agitation in favor of weighing the juice, but this entails considerable expense that the author does not consider always justified. The installation of measuring tanks on the capacity basis of 3 hectoliters net per ton of cane per hour (*i. e.*, 150 hectoliters, net, for 1200 tons daily capacity) eliminates occluded air to a negligible quantity, while a float of special size and shape enables the true level of the juice to be determined with exactness and simplicity. This is shown in Fig. 6. It is made of galvanized iron, conical at both ends, weighted with 9 $\frac{1}{2}$ lbs. of lead and provided at the top with a tube 2 inches long for holding a very light rod of wood, which in turn bears a double arrow and which is brought to a fixed point upon a scale.

The point A also serves as a definite spot from which to gauge the juice level for juices of different densities. The accompanying table shows the fluctuating juice level with varying Brix, the tank capacities being

Brix reading	Distance A, to juice level
21.3	17.3 cm.
15.6	15.9 cm.
9.6	14.5 cm.
4.8	13.2 cm.

calculated accordingly. These levels are actually determined by floating the instrument in diluted molasses of juice density in a tall cylinder. The float rises and falls in a cage. It rests for by far the greater part well below that part of the juice containing the unliberated air and allows no air to collect below it. It measures to within one-sixteenth inch under working conditions.

The specific gravity of the juice may be adjusted for varying temperature by the use of Gerlach's table.

Measuring tanks should be calibrated by weighing water into them until duplicate weighings agree within the polariscopic error as determined by the limits of the volumetric method using the Schmidt table.

(3) *Water of Saturation*.—The average temperature of this must be known in order to arrive at its weight, as it is probably invariably measured. Duplicate tanks serve the purpose of measuring, well, but a good water meter is sufficient, provided simple means are at hand for occasionally checking it, under actual working conditions.

(4) *The Bagasse*.—The weight of this, as determined by the formula Cane + Saturation Water — Raw

Mill Juice = Bagasse, is fully satisfactory, since the chemical control fails, in any case, where any one of the quantities is in error.

Stock Taking.—The short season requires frequent stock taking and the author recommends that this be taken once a week until it has been demonstrated that the factory is working normally, but after this, with cane work, once a month is sufficient for the fully detailed report. For this weekly check, advantage should be taken of a stop and all the products of the factory composited into one laboratory sample upon the basis of the several volumes, when one analysis and one calculation will give the desired information.

THE SUGAR ACCOUNT

All the sugar in the cane must be accounted for and brought up to a sum total of 100 per cent. The following form is a good general example.

	Per cent. basis of cane	Sugar in cane 100 per cent.	Per cent. basis of juice	Tons
General sugar account				
Sugar in first sugar.....	9.14	72.67	78.97	4070.5
Sugar in second sugar.....	1.11	8.84	9.59	494.5
Sugar in total sugar.....	10.25	81.51	88.56	4565.0
Sugar in press cake.....	0.06	0.53	0.58	29.6
Sugar in final molasses.....	1.16	9.22	10.02	516.5
Sugar in undetermined loss.....	0.10	0.77	0.84	43.3
Sugar in mill raw juice.....	11.57	92.03	100.00	5154.4
Sugar in bagasse.....	1.00	7.97	..	446.5
Sugar in cane.....	12.57	100.00	..	5600.9

In a full technical account, the above represents about 20 per cent. the data, the rest including averages of the analyses made of all the products, together with tons of cane ground, bags of the various grades of sugar made, time lost for different causes, data connected with the mill efficiency and the percentage yield of commercial sugars upon the basis of the cane.

The undetermined loss is due chiefly to the impossibility of accounting for all material involved in any undertaking.

There is loss from spilling, from inversion, long action of heat and errors in weights and measures with limits in accuracy of analyses. When this figure is 1 per cent. the total sugar in the juice it indicates good work, when it is 0.5 per cent. it is excellent work.

GENERAL METHODS

BRIX BY THE HYDROMETER.—All solutions up to 70° Brix are to be tested by the hydrometer directly, after the removal of air bubbles.

If the reading is not made at either 17 $\frac{1}{2}$ ° C. or 20° C. corrections will be made by means of tables to be found in any standard text-book.

DOUBLE DILUTION METHOD. [For products of over 70° Brix.]—The absence of cold water in tropical work precludes the cooling of solutions that have once been heated. The following method has been found most practicable: Use nickel-plated, copper beakers of such size that the fist may readily be introduced. Select two of about equal weight and place upon opposite pans of the balance; from the heavier, file or cut off the material around the upper edge until they exactly balance. With the beakers now upon opposite pans of the balance, in one place about 400 grams or any convenient quantity of the material; into the

other pour water until exact balance is secured; remove the beakers from the balance and pour the water of the one into the other containing the material; by means of the hand, mix the two until the last grain is dissolved; do not remove the hand until the operation is complete, in fact, endeavor to keep the hand equally submerged all the time.

Allow to stand until air has risen; take the Brix by the hydrometer, correct to standard temperature and multiply the result by 2. If the beaker used for water be only lightly greased within, it will deliver the water to the other to the last drop, thus obviating pouring back.

THE DILUTION TO 18 TO 20 BRIX.—For rapid control of the process of boiling, based upon the purity, all products will be reduced to uniform density within these limits before making the test. Simple as it seems, the average chemist is longer in learning to perform this test with unflinching accuracy than any other test in sugar manufacture, this being especially true with products containing grain in suspension. The fault lies in losing some of the material by spilling before all the grain has been dissolved or before the mixture is absolutely uniform.

(1) For products positively known to contain no grain: Select a cylinder 15 inches tall by 1½ inches diameter, having the upper edge of such a shape that it may be perfectly sealed by the palm of the hand; fill about two-thirds with water, pour in from about 110–120 cc. of the material, adding more water until within about 1½ inch from the top; seal tightly with the palm of the hand and shake vigorously until mixture is intimate; the result should always be a solution too dense rather than too thin; pour out a portion and add water if trial test shows too dense, mixing as before; continue this until proper figure is reached.

(2) For products known or suspected to have grain: Select two-liter enamelled cups of unbroken surface—these have no corners in which the grain may lodge and thus escape solution. Pour into the cup about 500 cc. of water, add about 200 cc. of the material and by means of the hand manipulate the mass until no more grain can be felt; transfer the solution to the cylinder and proceed as under (1) until the density is reduced to 18–20° Brix.

DRY SUBSTANCE.—In the cane sugar industry this is a purely empirical process, and close conformity to certain conditions is necessary to secure even comparative results. The breaking down of the levulose molecule at temperatures above 80° C., the oxidation of non-sugars, the formation of acids that in turn produce more invert sugar which continues to decompose, make it impossible to dry to constant weight at atmospheric pressure, therefore a vacuum should be employed: when the temperature is held at 70° C., the vacuum should not be under 25 inches and a slow current of dry air allowed to pass through; weigh every 2–3 hours until constant in weight.

In the absence of any vacuum the following method may be used. It is based upon the official method of the Association of Official Agricultural Chemists,

Bull. 107 (revised), U. S. Bureau of Chemistry, p. 64.

Place in a light crystallizing dish, provided with a watch-glass cover and stirring rod, 25 grams of broken glass in quite uniform pieces the size of coarse sand and washed free from dust. Dry quickly at 120°–140° C., cool in a desiccator and weigh. Of sugar, take 10 grams; of molasses, 5–6 grams; of mill raw juice, 35 grams. Dry for exactly 10 hours at 98°–100° C. (boiling-water jacket). The time for drying the juice should begin with the disappearance of the water.

SULFATED ASH.—About 3 grams of sugar are used and a proportionate amount of other products; if moisture exceed 25 per cent., as in cane juice, the water must be evaporated on the water bath. The true ash is calculated by multiplying by the factor 0.9.

CONDENSED WATERS.—These include all the main hot water collectors, the pan and evaporator tail-pipes. To be tested for sugar with alpha-naphthol. Some form of continuous sampler is advised.

The Test.—(Fruhling and Schultz, *Anleitung*, p. 166.) To 2 cc. of the suspected liquid add 5 drops of a 20 per cent. alcoholic, sugar-free, alpha-naphthol solution, then 10 cc. of purest sulfuric acid and shake thoroughly. With 0.1 per cent. sugar the color is so deep as not to be transparent; with 0.01 per cent. a bright red wine.

Boiler Water.—Determine the acidity of the boiler-fed water and the alkalinity of the boiler water every 12 hours.

For the test, take a small amount from each boiler in service, titrate with standard acid (1 cc. = 0.001 CaO), using methyl orange as indicator. Report as grams CaO per 100 cc. Report number of pounds soda-ash used per 24 hrs.

PREPARATION FOR CLERGET TEST AND INVERT SUGAR. *Juices.*—Determine the sp. gr. Clarify 500 cc., strained and air-free, with neutral lead acetate sol. (50° Brix); dilute to 550 cc., shake well and filter. Make the direct reading at as near 20° C. as possible. To about 150 cc., add ignited Na₂CO₃ to scant phenolphthalein alkalinity, stir and let stand 15 minutes; filter. Use exactly 75 cc. for Clerget by the Herzfeld inversion method. Use about 5 cc. for invert sugar test.

Molasses.—Wash 2½ normals into a 500 cc. flask, clarify with solution of basic lead acetate, mix, rotate to expel air, dilute to the mark and filter; collect 250 cc., neutralize with glacial acetic acid, double the amount of acetic acid; throw the filter and precipitate into the clear liquor, mix thoroughly and again filter. Polarize and multiply by 2. Remove the lead with Na₂CO₃ and proceed as under Juices for Clerget Test and Invert Sugar, using 15–20 cc. for the latter. True sucrose should be calculated by the following formulae.

Juice	Molasses
26 × invert pol. + direct pol.	Direct pol. — invert
68.18 sp. gr.	pol. (2.67)
142.66 — 0.5 t	142.66 — 0.5 t

Herzfeld's Inversion Method.—This will be found in

detail in any standard work. After inversion is complete and while still in the water bath, add 1 gram powdered zinc, heat for another 5 minutes, pass through cotton, wash the cotton until 100 cc. is obtained at 20° C.

Invert Sugar Determination.—To exactly 10 cc. of Fehling's solution, blue, and 10 cc. of Fehling's solution, white, in a 250 cc. flask, add the solution under test and enough distilled water to make 50 cc. Boil cautiously upon a square of asbestos, having a central hole, for 2 minutes, then cool quickly. Add 10 cc. of 20 per cent. solution KI, rotate, add 10 cc. of 25 per cent. H_2SO_4 , then nitrate with $N/10$ thiosulfate. Work rapidly throughout, running in by 3-4 drops at the end.

Run a "blanc" upon the Fehling solution, under precise conditions of analysis to determine its value in terms of thiosulfate. Use the table of Meissl¹ and Hiller to calculate results. Careful determinations by several chemists have shown that not all of the copper present can be accounted for with cane products, and the following table of factors was been worked out:

$$\times 20.82 = 0.1324 \text{ gram Cu, } \frac{0.1324}{2} = 0.0662 = Z.$$

$W = 8.275$ grams material taken for determination. Polarization = 10.08. $0.0662 \times 100/8.275 = Y = 0.8$ per cent., $100 \times 10.08/10.08 + 0.8 = 92.7 = R$. $100 - 92.7 = 7.3 = I$. Since 20 cc. of Fehling's solution were used instead of 50 cc., $Cu/2$ or 0.0662 gram must be multiplied by 2.5 to find the factor, F , which equals 0.165 gram Cu. By the Meissl and Hiller table, factor = 53.1. Hence $0.1324 \times 53.1/8.275 = 0.85$ approximate invert. Referring to the above table of corrections results in that of 1.016. 0.85 per cent. $\times 1.016$ gives 0.864 per cent. corrected.

765 WESTMINSTER ROAD
BROOKLYN, N. Y.

STERILIZATION OF WATER SUPPLY AT TRENTON

By H. C. HOTTEL¹

Received January 6, 1913

Statistics issued by Dr. A. S. Fell, Health Officer of the City of Trenton, show that there have been 100 cases of typhoid fever in the city during the year



CHART SHOWING CASES OF TYPHOID REPORTED IN TRENTON, BY WEEKS. CASES IN 1911 ARE SHOWN BY THE BROKEN LINE; CASES IN 1912 BY THE SOLID LINE

TABLE OF INVERT SUGAR FACTORS

For use where the copper reduced is determined by difference

	Juices		Sugars		Molasses					
	C	F	C	F	2	32	2	46	2	2
Cc. decinormal thiosulfate used	I	I	I	I	I	I	I	I	I	I
5	0.981	0.928	0.950	0.926	0.996	0.934	0.960	0.956		
10	0.998	0.919	0.966	0.961	1.013	0.980	0.983	0.988		
15	1.007	1.013	0.989	1.011	1.017	1.011	0.988	1.010		
15.5								1.015		
20	1.016	1.048	1.016	1.021	1.020	1.032	1.001	1.001		
25	1.045		1.030	0.963	1.022	1.047	1.002	0.971		

Example.—Used in "blanc" titration, 27.75 cc., in back titration, 6.93 cc., net utilized, 20.82 cc. 0.06636

¹ Spencer's "Handbook for Cane Sugar Manufacturers," pp. 129, 130.

1912. For the previous five years the number of cases averaged over 250 annually. The total for the year 1911 was 302 cases. The highest number of cases reported in any one week in 1912 was 7 while the highest number in 1911 was 24.

The drop in the number of typhoid cases is attributed to the use of calcium hypochlorite to sterilize the drinking-water supply, raw Delaware River water. The chart shows in a graphic manner the decrease in typhoid.

The following table shows the wide range between the two years. In 1912 there were only nine weeks in which more than three cases were reported while in 1911 there were 33 weeks in which more than this number were recorded.

¹ City Chemist, Trenton, New Jersey.

Cases each week	1911	1912
0	3 weeks	12 weeks
1	6 weeks	13 weeks
2	7 weeks	7 weeks
3	3 weeks	11 weeks
Above 3	33 weeks	9 weeks

The sterilization plant was installed in Nov., 1911, at a cost of \$4,500 and has been in continuous operation since that time. It is not intended, however, to always treat the water in this manner, as plans have been completed and the contract awarded for the erection of a mechanical filtration plant, with a capacity of 30,000,000 gallons of water daily at a cost of \$330,000.

When first installed the hypochlorite plant was under the supervision of the New Jersey State Board of Health but in March, 1912, the city took charge of the operation of the plant.

The hypochlorite purchased averages about 35 per cent. available chlorine, and treatment was begun with a strength of 0.4 part to the million of available chlorine. This was found to be insufficient and was later raised to 0.8 part and during the year 1912 has varied from 0.7 to 1 part per million with a daily pumpage of about 20,000,000 gallons. In commercial terms this means that 17 to 24 pounds of calcium hypochlorite has been added to every million gallons of water pumped.

Tests of the treated water show a material decrease in the number of bacteria. Ninety-eight per cent. of the tests for colon bacillus, in one cc. of the raw water gave positive results. In the treated water the positive tests for colon bacillus in one cc. have averaged 20 per cent. The average 20° bacteria reduction per cc. of water has been 94.1 per cent.

The hypochlorite plant consists of a small two-story frame building. The lower floor is divided into two rooms, a chemical storage room and a machinery room; the second floor comprises the operating room and office. The machinery and apparatus consists of two chemical dissolving tanks, two chemical solution tanks, one orifice tank and one receiving tank, the last-named tank being connected by a supply pipe to a grid located in the sluice gate manhole in the intake, at a point just before the intake enters the pump well at the main pumping station. From this point the water is pumped to a 110,000,000 gallon distributing reservoir, it requiring about 90 minutes to reach the reservoir from the pumping station. The chemical is dissolved to a 2 per cent. solution and the orifice controls the rate (in gallons per minute) at which the solution is added to the raw water. The plant is under the supervision of Chief Engineer Lenox of the pumping station and, as it is necessary to have some one in constant attendance, it requires the services of three men working on eight-hour shifts.

That the hypochlorite treatment is being used extensively in drinking-water supplies of American cities is attested by the report of the Ohio State Board of Health.¹ It states that information has been received in regard to the drinking-water supply of 99 cities of over 25,000 population in the United States,

and that 40 per cent. of these cities are using hypochlorite to purify the water.

THE DETERMINATION OF MINERAL AGGREGATE IN BITUMEN PAVEMENTS

By C. C. O'LOUGHLIN

Received November 21, 1912

The experiments described below were carried out as a comparison of the filtration and centrifugal methods for the determination of mineral aggregate in bituminous substances.

The following samples were used for both methods:

Refined Trinidad asphalt	51.60% bitumen
Refined Bermudez asphalt	96.22% bitumen
California "D" grade asphalt	99.94% bitumen
California "G" grade asphalt	98.86% bitumen

The Filtration Method.—Ten grams of the asphaltic mixture were weighed and placed in a 2½" funnel, which contained a 9 cm. Schleicher & Schull No. 597 filter paper; a 250 cc. Erlenmeyer flask was used to catch the filtrate.

Carbon bisulfide was run onto the sample until absorbed, but no more, and allowed to stand until it softened and settled into the filter; it was washed again until the solvent nearly filled the filter. This operation was repeated until the filtrate came through clear and then finished with two washings of petroleic ether. The latter operation was found necessary to clean the aggregate of some of the lighter oils, which seemed to remain even after repeated washings with carbon bisulfide.

The aggregate was allowed to drain and when dry brushed onto a watch-glass. The filter paper was placed in a porcelain crucible, burned at a low heat, and then added to the main residue on the watch-glass. The combined samples were dried, cooled in a desiccator and weighed, the weight of residue being the aggregate and the difference being the bitumen.

The above method was found to take from 4 to 10 hours, and in some cases as long as 20 hours. This method used about 250 cc. of solvent.

The Centrifugal Method.—In this method the Dulin Rotarex, designed by R. S. Dulin, Chemical Engineer of the City of Portland, Oregon, was used. This apparatus consists of an aluminum bowl receptacle for the sample, which is 3½" in diameter and equipped with a suitable cover; the cover is fastened on by means of a funnel-shaped screw, through which the solvent is added; this also allows the escape of gases. The above is enclosed in a copper shell, provided with a spout at the bottom side, through which the waste liquors drain; the shell is provided with a two-piece cover, the smaller one being removed to add additional solvent. The machine is run by electric motor directly underneath. The filter of proper diameter is placed between the bowl and cover, and when the machine is in operation the solvent is thrown to the sides, passing through the filter, carrying with it the soluble matter.

Fifty grams of sample were placed in the bowl, the filter put in place, the cover fastened on and 50 cc. of solvent added; the machine was rotated until

¹ Ohio State Board of Health, Monthly Bulletin, Oct., 1912.

the solution ceased to run out of the spout. This operation was repeated and a final extraction with 25 cc. made; the cover was removed and the aggregate allowed to stand in the bowl for about 2 minutes; it was then brushed onto a watch-glass and finished as in the filtration method, burning the filter if necessary, which was not very often the case.

It was found that the centrifugal method on an average of several samples took from 10 to 15 min-

utes for the complete determination, and that the results check very closely, due to using a large amount of sample for each determination and thereby reducing the error. It was not necessary to finish with petroleic ether, as the results did not differ to an appreciable amount when using ether after the regular extraction. The average amount of solvent used for a determination was 125 cc.

205 COLMAN BUILDING
SEATTLE, WASH.

ADDRESSES

THE PROBLEM OF INTERNATIONAL CONGRESSES OF APPLIED CHEMISTRY

By BERNHARD C. HESSE¹

The object of the following is to present in concise and impersonal form some of the lessons that seem to me to be read out of the experience obtained in preparing for and in participating in the conduct of the Eighth International Congress of Applied Chemistry. I am persuaded that these notes may be useful, because of the opinions expressed by most of my friends with whom I have discussed the subject, and to whom I have presented my views.

In reading these pages the fact must not be lost sight of that they in no wise deal with the social, the factory-inspection, nor the private entertainment side of such a Congress, nor with anything that in any way deals with any "host and guest" aspect of these Congresses, all of which I regard as with perfect propriety not a matter of any concern whatever to these Congresses as an institution; they are the pleasure and the reward of the host country alone. This article is limited strictly to the outline, preparation and conduct of the scientific side—the actual hard work of the Congress about which all other functions are supposed to cluster. This work is held out as being the real justification for the existence of these Congresses and constitutes their real merit in aiding the progress of mankind.

My own conclusions, based upon what is contained in the succeeding pages, may, in part, be summed up as follows:

I. The International Congresses of Applied Chemistry of the past have been loaded down with such an overwhelming proportion of extraneous matter that their true business has been entirely submerged. The only remedy lies in curtailing such matter and limiting the activities of the meetings to matter of international and debatable character all pre-arranged, with leading discussions in print and the whole matter prepared for *viva voce* discussion.

II. Sectional meetings should be on alternate days and the intervening days be used by sectional secretaries and participants in discussion in definitely making up the record of the meetings of the preceding days; all matter not in the hands of the sectional secretaries within a reasonable time, say, three working days after the close of the Congress, should be denied admission to the printed record.

III. All manuscript *must* be typewritten and all other requirements of the printer fulfilled by all authors, otherwise the papers should be returned by the Committee to their authors.

IV. The only way that the persistent and thoroughly correct demand of members for rapid delivery of the printed proceedings can be complied with is to require all participants to be prompt in supplying their manuscript; rapidity of execution requires efficiency in organization and contributing members are part of such an organization; they must all discharge their respective duties at the same efficiency rate that they expect the officers

in charge to achieve; no committee can print from nothing, nor can it proceed any faster than the slowest contributor.

V. The demands made upon the Congress for the treatment of scientific matter have grown out of all proportion to the financial ability of the Congress; prudence and caution as well as a decent regard for financial propriety all demand that that part of the undertaking of the Congress be cut down to a dimension commensurate with its income.

The reasons for these and other conclusions will be made clear as this article proceeds.

Inspection of the Reports of all preceding Congresses, inclusive of the Eighth, discloses an evergrowing tendency to increasing bulkiness, with little or no increase in the efficiency or ripeness of the actual, crystallized work of these Congresses; namely, the discussions and the resolutions offered to and considered by the Congress meeting as a whole in its last session and the Reports of Commissions or Committees created at a preceding Congress and directed to report at a subsequent Congress.

Everyone must be struck by the enormous amount of material brought together at the Eighth Congress. On suitable examination all will, no doubt, agree that more than 90 per cent. of all such material (however valuable *per se* it may be) is not fitted for nor adapted to discussion in a meeting where international interests are supposed to be primarily or almost solely involved; also that these 90 per cent. would have been written and published without the stimulus of such a Congress, in the publications now so plentifully provided all over the world. The final result is that, in an endeavor to do seeming justice to the great bulk of material offered, the real and important work of the Congress (the formulation of an expression of opinion on the part of the Congress on certain topics of international import, scope and interest) is drowned while resolutions and reports are put through hurriedly and without due consideration by the various sections, trusting to the International Commission or to the Congress itself to take care of any imperfect work.

Clearly, it is not the object of these Congresses to provide merely another vehicle of publication for papers that would be written and published without the stimulus of the Congress, nor do men go to the expenditure of time, money and effort to attend such gatherings merely to hear papers read that would reach their library desks automatically. The object of these Congresses must be to bring forth a class of communications and results which cannot be created nor accomplished by the societies, associations and publications, now so plentifully at hand. The results that these Congresses must be intended for, are those for whose accomplishment direct personal contact and direct attrition of minds of men of different and differing opinion on debatable questions are prime requisites and essentials so that out of these various opinions some order, some system, some agreement, some progress may arise. There is very little to be gained by discussing a paper which merely tells you the physical or chemical constants of a limited number of substances, cer-

¹ Secretary of the Eighth International Congress of Applied Chemistry held in New York City, September, 1912.

tainly not enough to make it worth the while of any considerable body of men to travel across oceans and continents to attend the reading of such papers.

In addition to these discussions of debatable questions there is the coöperative work needed for the solution of problems of international importance and the receipt and discussion of reports thereon by the Commissions appointed by preceding Congresses; like the resolutions mentioned above these too are caught in the maelstrom of papers, suffer from want of discussion and do not receive that attention which they require and merit. Yet these resolutions and reports are the *only* work that depends upon and requires such gatherings. The world does not now have ample volunteer and non-governmental machinery for them, and they have not held that prominence and that importance in past Congresses which their potential value justifies and demands.

It is easily manifest that past Congresses have not provided for the Commissions reporting to them that machinery best adapted to the attainment of worth-while results, nor have they given to the results reported that attention and publicity to which their history and origin entitles them. To serve on such a Commission or Committee is wholly a labor of love; the money grants made by the Congress are wholly insufficient to give proper publicity to the *results*, not to speak of the expenses of organization and the needed clerical work if the task is to be well done. When such a Committee does report, its reports are not accessible to the members of the Congress-at-large. It is very easy for a Congress to say to a certain Committee that such and such work shall be done by the time the next Congress meets, but it is anything but easy to accomplish that thing in the allotted time and present it in a form accessible for discussion; furthermore, when it is presented for discussion those receiving the report should be acquainted with its nature sufficiently in advance to enable them to prepare a useful, helpful and creditable discussion and criticism, both destructive and constructive, of the work on which so much time, labor and thought have been spent. Perfunctory acceptance or perfunctory discussion or perfunctory discontinuance of labor voluntarily assumed in the belief that it is of wide and general importance and thereupon conscientiously performed with considerable sacrifice of time, effort and labor is not conducive to causing busy men to expose themselves to such sacrifice for so unsatisfying if not distinctly discouraging reward or treatment. If such treatment continues, there can be but one result—men less qualified for the work will undertake it and reports of lesser and lessening value will be produced. If the value of such reports is to increase and these Congresses are more closely to approach the *only* field of real international usefulness open to them, then more thought and more reflection must be given to the outline of the work to be performed when a Commission or Committee is created, more consideration and discussion must be given to the report when ready, and the report itself must be more widely distributed and much more in advance of the meeting than heretofore; besides more financial assistance must be given; the same is true of resolutions expressing the conclusion or consensus of opinion of the Congress on any debatable subject or topic.

Of the 18 reports by Committees or Commissions that should have been made to the Eighth Congress only 2 were so made; further, of 25 resolutions adopted by Sections only 9 were placed before the Congress because of the failure of the sponsors of the remaining 16 to perform their respective duties.

Now, how can this be done? Merely to point out a fault without suggesting a remedy is an easy thing to do. I fully realize how difficult it is and perhaps how egotistical it may seem to propose such a remedy; nevertheless, I run the risk of error and misunderstanding and propose what seems to me to be one feasible plan, but I must not be understood to mean that

I regard this as the *only* or as a *complete* solution. It is brought up for the purpose of discussion in the hope that something will result from it which may in the future prevent these Congresses from falling within themselves on account of their unwieldiness, bulkiness and their poverty in results actually accomplished.

The plan is as follows:

- I. Abolish all papers on promiscuous subjects.
- II. Reduce the number of sections to four, say
 1. Inorganic.
 2. Organic.
 3. Analytical
 4. Administrative.
- III. Confine the work of each section to a stated program mapped out in ample time in advance of the meeting and limit its work to deliberation on reports submitted and resolutions to be proposed to the Congress as a whole.
- IV. Have sectional meetings on alternate days only, *e. g.*, Monday, Wednesday and Friday with the Final General Meeting of the Congress on Saturday afternoon. Tuesday, Thursday and Saturday morning to be given up to sight-seeing, works inspection and social and other matters generally; this time must also be used by the sectional secretaries and participants in discussion in properly assembling and writing the minutes of each meeting and in preparing the proper matter for the daily paper of the Congress giving the text of the resolutions finally adopted by each section.
- V. Give Monday, Wednesday and Friday afternoons, if desirable, to general lectures of the type heretofore held; these would provide ample opportunity for the broad presentation of chemical topics to the Congress and to the public in general.
- VI. Hold Sectional Meetings from 10 to 12 and from 1 to 3 and general lectures at 4.

The topics on which resolutions are to be proposed to the Congress should be determined by the Committee in charge of the Congress in any way suitable to it; one way might be to present the Committee's views to each of the societies, institutions and associations represented by delegates at the last preceding Congress and to ask for criticisms of the list of topics so submitted and for suggestions as to those fitted to take part in the leading discussions; the suggestions of the Committee together with those received from these above defined organizations with respect to all topics should be sent to the technical press on a stated day as well as those left open for further criticism by the general chemical public until a certain other stated day. The Committee in charge of the Congress should select from all these topics those that it deems suitable for consideration and announce their definite selection together with their numerical designation, their assignment to sections and their places upon the program *not less than eighteen months in advance of the meeting* and send such statement to the various organizations and to the technical press. Further, this Committee should select for each debatable topic definitely put upon the program one individual to discuss the topic broadly but concisely not to exceed 4,000 words, and then assign to each of two different view points of the subject one man who shall not exceed 2,000 words (all those suggesting topics should also suggest the names of those who might be in position to discuss them to advantage, but these names should not be made public); the leader's article should be ready 120 days before the Congress meets and be sent to the other two writers, whose two articles should be with the Committee ninety days before the Congress meets. These individuals should be selected and announced one year before the Congress meets. These three contributions should each carry a proposed resolution or resolutions for submission to the relevant section. Ninety days before the Congress meets no further suggestions of topics for resolution or report should be received and no further memberships or delegations accepted. This period of ninety days will all be needed to enable the Com-

mittees of the Congress to make proper preparation for the prompt despatch of business and the proper social and other diversions; ninety days before the Congress meets all foreign central committees and organizations should telegraph the Congress Committee the number of members in their jurisdictions and how many of them will probably attend the meeting together with the probable number of accompanying ladies and should follow this telegram up with a typewritten list, in duplicate, of all members in their respective jurisdictions together with the post-office address of each member; the same should be done with respect to those members who have declared their intention of attending and so far as possible with their addresses while attending the Congress.

Ninety days before the Congress meets all reports to be presented should be in the hands of the Committee; these reports together with all the discussion papers, should then be printed and put in the mail for distribution to members of the Congress sixty days before the Congress meets together with a copy of the program in full, giving the date and time of day when each topic or report is to come up for action. In this way every member would have foreknowledge of all the principal points at his home not less than thirty days before the Congress meets and all who are interested would have ample time to prepare creditable and really valuable criticisms and discussions of definite subjects and topics; it might also be feasible to permit absent members to send in their criticisms in writing for presentation to the section in charge, but this suggestion seems to me to be of doubtful value.

The Committee in charge of the Congress would, of course, add to this printed volume a list of all the topics presented to it as subjects for discussion and which it did not accept so that the various sections could consider them also in laying plans for the succeeding Congress; after they had placed their recommendations with the Congress, the latter, at the meeting of Saturday afternoon, could have the benefit of all these suggestions and of the various valuations placed upon them in deciding what should be, in part, the leading topics for the next Congress.

At the sectional meetings where resolutions and reports are discussed, suitable stenographic or reportographic minutes should be taken and after proper editing printed in a supplemental volume together with the final action on each topic, resolution or report. This would result in a compact, concise and clear exposition of the real work of the Congress, free from all the distraction of extraneous and promiscuous papers; of smaller dimensions than its predecessors, doubtless and necessarily, but therefore all the more valuable and meritorious.

In the program proposed there are provided six meeting periods for each section, or a total of forty-eight meeting hours. If, in each two meeting hours, one good resolution or expression of consensus of opinion can be adopted; or one good report received, thoroughly discussed and further feasible work mapped out; or a new commission established with ample and explicit working directions; the real and only field of international congressional work will have been covered in a fairly efficient manner and progress towards complete accomplishment and achievement of that real work will have been made. In this manner the attention of those in attendance at sectional meetings will be riveted on one, and only one, topic at a time; having two hours to make something out of the predigested subject-matter, with no further chance to consider it, the probabilities are that proper consideration will be bestowed upon these subjects with results bound to be more nearly worth while than any in the past; at any rate, if under these conditions worth-while results be not accomplished the responsibility for such non-accomplishment cannot be shifted to the presence of distracting papers. Each section would be known as being solely and alone responsible for the good or bad quality of the work turned out.

The responsibility of selecting worth-while topics, properly assigning them to sections and disposing of them in the program

would be wholly upon the Committee in charge of the Congress; with only twenty-four items of business to arrange, it is clear that the task of selecting good and worth-while topics and placing them in the program is not so difficult as it might, at first glance, appear to be. Certainly, not so difficult and unsatisfactory as trying to arrange 789 papers to suit as many authors and several times that number of auditors.

It may be objected that this would greatly reduce the attendance at the sectional meetings; if it reduces that attendance to all those actually interested and prepared to take part in the work no possible harm can come to the Congress and its work.

From the report of the Secretary of the Eighth Congress (see p. 344, this issue) the following table, which is self-explanatory, is deduced:

	Papers presented	Papers read by authors	Per cent. of papers not read by authors	Attendance	Participants in discussion	Per cent. of attendance represented by participants in discussion
Sectional meetings	546	286	47.6	3,956	610	15.42
Joint sessions(a)	157	96	37.2	2,650	250	9.4
Grand total	703	382	45.6	6,606	860	12.9

(a) Not including three joint sessions at which discussion was not invited.

A total of 789 papers was presented to the Eighth Congress; of these 703 were presented to the meetings by the authors' representative or by title, and 86 were not presented to the meetings in any form whatever, although printed in the final report. Therefore, almost half the authors did not appear to defend or sustain their papers, 11 per cent. did not even offer their papers to the meetings and only about one-eighth of all persons in attendance made any remarks on the papers presented; surely the remaining seven-eighths might just as well have been elsewhere so far as the real work of the Congress is concerned.

At the closing general meeting of that Congress fewer than 400 were in attendance and of these only 15 or 3.75 per cent. took part in the discussions, *i. e.*, less than one per cent. of all who had registered took part in the final deliberations of that Congress. It further appears from the same report that eighty of the offered opportunities for meeting were not used and that not to exceed 217 of the 530 sectional meeting hours placed at the disposal of the Congress were utilized. Out of 217 actual meeting hours only 169 were used for reading and discussing papers, leaving 48 hours, at most, for the consideration of the total of twenty-five resolutions introduced and for the transaction of such other business as may have engaged the attention of the respective sections. It is perfectly safe to say, however, that these forty-eight hours were not nearly all used for discussions of resolutions.

It therefore seems not unreasonable to expect that a grand total of forty-eight hours of work devoted to a grand total of twenty-four different topics by four different sections, will produce a concentrated and compendious and very much worthwhile piece of work—one in which the real matter is not buried under a mass of irrelevant matter, however interesting and otherwise valuable that matter may be.

This concentrated and classified program of the scientific work need in no way whatever interfere with any other of the functions incidental to such Congresses; quite the contrary, men who have undergone such concentrated and responsible work are all the more entitled to relaxation and enjoyment, and are all the more entitled to the privileges of factory and works inspection; they will have earned them many times over.

This plan of procedure would not only produce a final report of greater value, accessibility and utility than any of its predecessors, but would materially lessen the labors of the Committee in charge of the Congress and permit it to concentrate more

thoroughly on the actual and vital things needful for the accomplishment of the proper work of the Congress because these would thereby be greatly lessened in numbers and scope; necessarily with that it would prevent what cannot be, in the light of the preceding, anything but a waste of money and substance. The printing of 90 per cent. of needless matter of the Eighth Congress called for the use of upwards of fifty-four tons of perfectly good white paper (representing in value 1,080 membership fees) and this, to all practical intents and purposes, is a waste of just so much good material and membership fees, a thing which chemists, above all other professionals, should not tolerate nor encourage. I am in position to know that this unnecessary printing and the labor connected with the collection and handling of these papers, cost the Eighth Congress substantially 6,600 membership fees, whereas the paid-up membership was only 4,163 or roughly 63 per cent. of these needless expenditures. If the policy that seems heretofore to have governed Congresses continues, these needless expenditures of time, labor, money and effort will increase and sooner or later assume far greater relative proportions with respect to income from memberships and therefore must inevitably destroy the support given these Congresses by chemists-at-large; finally these Congresses must of necessity disappear—a circumstance to be regarded as nothing less than a calamity since the field for these Congresses does exist and there is need of the work they can perform.

Needless to say, no business enterprise could survive such disproportion between income and outgo and no institution operated on such inefficient lines has any real claim to support, encouragement or consideration from any source whatever. These Congresses have now passed through eight meetings and the institution as a whole is nineteen years or more old; it is not unreasonable to expect that a definite proper policy as to scope, commensurate with the income of and the actual interest in the institution, should be adopted. In this connection it may be useful to refer to a paper by Walter F. Reid (*Journal of the Society of Chemical Industry*, 1907, 75) in which he gives the total cost of some of these Congresses and their memberships.

	Total outgo, expressed in membership fees	Income, expressed in membership fees	Deficit, expressed in membership fees
1897 Vienna.....	782
1900 Paris.....	1,200	1,751	551(a)
1903 Berlin.....	15,000	2,533	12,467
1906 Rome.....	8,160	2,375	5,785
(a) Surplus.			

(It might be helpful in framing a definite policy to ascertain just what things caused the surplus of 1900 to be thereafter turned into a deficit in each case greater than the total outgo of all preceding Congresses.)

Corresponding figures for the Seventh or London Congress of 1909 are not available. In the Eighth Congress the expenses for printing the proceedings were 7,000 membership fees, for propaganda 2,000, for stenographic and recording service 500, for registration, daily journals and delivery of original communications 300 or a total of 9,800 membership fees, leaving for really legitimate strict Congress-business expenses a deficit of 5,628 membership fees. It is this sort of a deficit that calls for immediate, serious scrutiny and attention; unfortunately the Berlin and Rome figures are not capable of being distributed over strict Congress-business expenses on the one hand and expenses which are chargeable to hospitality, entertainment and the like, on the other; these latter are certainly not matters of concern to the Congress but the former most certainly are and they are the only ones here considered or in any way referred to.

The only remedy seems to lie in following the old adage: "Cut your coat according to your cloth" and that is precisely what the above proposed plan is peculiarly adapted for. The amount of preparatory work would be greatly diminished and also the preliminary printing; the amount of printing needed

throughout would be greatly reduced. Based upon the experience of the Eighth Congress, it is safe to say that all the needful preliminary work could be done for 600 membership fees; that all the printing necessary, all expense of reprints and placing of the volumes with the transportation lines and all strictly Congress work during the meeting could be done for 2,500 additional membership fees, i. e., the entire expense of the Congress would be covered by 3,100 membership fees. Had the American Committee been at liberty to adopt some such plan as that proposed, it is safe to say that there would have been a fund left of substantially 1,000 membership fees. What effective and useful work that sum of money would have enabled the Eighth Congress to initiate for the Ninth! What an entirely different economic position these Congresses would then occupy! Instead of being dependent they would be independent; instead of justifying their existence by glittering generalities and of obtaining support and financial aid by appeals to national or civic pride they would be their own justification; the honor of being hosts to them would be spiritedly sought after; places on the Committees or Commissions to report to subsequent Congresses would be regarded as prizes to be struggled for and coveted and not, as now, accepted in a spirit of sacrifice for the good of the cause! The fact that all the organizations and individual chemists in the different countries would have a part in shaping and directing the program would greatly stimulate interest in the Congress by making each feel a direct interest. No doubt the Committee in charge would not be put in the embarrassing position of having 70 per cent. of its invitations to such organizations ignored and only 25 per cent. accepted; it would be spared the immense labor of sending out over 17,000 letters soliciting contributions of papers to the Congress; it would be relieved of writing up its aims and hopes from over 400 view-points and sending them out to the extent of over 300,000 pieces; it would be relieved of sending out over 120,000 application blanks for membership and receiving only one-thirtieth of them back as effective applications.

It is difficult to conceive that, among the thousands upon thousands of chemists the world over, 4,000 of them would not discern it to their advantage to subscribe the same membership fee, as heretofore, to support an enterprise of the kind outlined; the volume or volumes containing the work of the Congress would be absolutely unique in chemical literature and would perform a function not now performed, which cannot be otherwise than of use to all chemists. In so subscribing they would make it self-supporting and therefore self-perpetuating; its influence would be capable of continuous and powerful exercise and could be made to develop continuously and steadily along preconceived and clearly marked lines being controlled by a continuous and continuing policy, itself capable of adaptation to changing conditions, none of which properties are possessed by the Congresses of the past.

In view of the fact that 11% of all the papers printed were not read at the Eighth Congress even by title and that on the average only 44.5% of those in attendance at the Congress were present at the reading of those papers, that the discussion of only 22% of all the papers presented was finally accepted for printing, it must be apparent that the reading and discussing of papers form a very small part of the justification of these Congresses, nor can any great proportion of this justification be credited to the reports and resolutions, for less than 22% of the time actually spent in meetings could have been used at the Eighth Congress for the discussion of such resolutions and reports, and only 36% of all resolutions discussed in Sections ever reached the Congress itself.

At the Seventh Congress only 11% of all papers read were discussed and only 30% of the members in attendance at the Congress were present at the reading of papers.

Clearly, there must be some other justification in the minds of

those attending these Congresses than the reading of papers and discussing of reports. What can it be? The Eighth Congress planned to have a "Special Interests Registration Bureau" where attending members who desired to exchange information on special subjects could register and be placed in communication with others interested in the same specialties. Before carrying out this plan the prospective members were asked their opinion on this point at p. 12 of the Preliminary Announcement of March 6, 1911, of which 65,000 copies in 5 different languages were distributed throughout the world. They were asked to say if they cared for that kind of a bureau and if so what divisions and subdivisions they desired. The result was exactly three responses—one was indifferent and the other two thought it might be a good thing. It would seem, therefore, that personal interchange of opinion and information arranged and provided for in orderly, thorough and systematic fashion is likewise no justification for these Congresses in the minds of those attending.

Again less than 10% of the attendance participated in the excursions and factory visits, so these cannot form any great part of the attraction of these Congresses.

The Eighth Congress has therefore definitely determined that papers, reports, personal interchange of information, excursions and factory inspection are not singly nor collectively any very great determining factors in inducing attendance upon these Congresses, and the puzzle of just what does constitute this real attraction and justification to those in attendance is passed on to the Ninth Congress in the hope that a correct and positive answer to it will then be obtained.

In the event that it should be considered unwise or not feasible to alter the policy governing the Congresses, experience with the Eighth Congress has shown that certain requirements and obligations, compliance with which has heretofore been left optional with members, should be made obligatory and mandatory.

1. Members should be *obliged* to have their names and complete post-office addresses typewritten or legibly printed by hand in their applications; writing should be absolutely barred for this purpose; to decipher the slovenly and indistinctly written applications for the Eighth Congress took four peoples' time for six weeks and cost 1.5 per cent. of the total income of the Congress from membership fees. It is simply ridiculous and absurd to place such a burden so willfully and recklessly upon a working staff and a Congress Committee both of which have other and more important things to occupy their attention. All applications not so made out should be rejected until so simple a requirement is complied with. Each member's own application should be so clear that it should be used for printer's copy direct.

2. Author's manuscript *must* be typewritten and in duplicate, both as to full paper and abstract, and all figures, drawings or illustrations must also be in duplicate. Handwritten manuscript is not only archaic but most difficult for a printer to follow. All manuscripts should be provided with a protective front and a back cover and firmly fastened together, with each page numbered; the places that separate drawings are to occupy should be clearly indicated; each drawing should be clearly numbered and the same number should appear at the space in the manuscript where the drawing belongs. Original and duplicate should not be sent in the same, but in separate packages; they should not be rolled or folded but should be sent flat; the printer can then set from the original and proof-read against the duplicate; in this way danger of delay, owing to loss or defacement of copy, can be avoided. Each document should bear in type-writing on the outside—the author's name, the full address to which reprints are to be sent, the number of reprints wanted, the number of the author's or authors' Treasurer's receipt for membership in the Congress, the number of pages in the docu-

ment, the number of separate drawings, if any. All drawings should be in india ink on white paper or possibly tracings on tracing cloth; blue-prints should not be sent for there is no generally adaptable method for reproducing them. The redrawing of blue-prints and slovenly or improperly made drawings cost the Eighth Congress 1.5 per cent. of its income from membership fees. Further, the author's front cover page should indicate all the different ways the title of the paper is to be indexed and cross-indexed in the final index to the Report; if the author needs facilities for an exhibition lantern and what size slides he proposes to use; if he wants experimental facilities and what; if he needs space for exhibits and how much.

It is discreditable that so many authors, as actually did in the Eighth Congress, should send manuscript slovenly written, not paged nor fastened together, without the author's post-office address, the number of reprints wanted, the number of their figures and without showing where the figures belonged in the text and with blue-prints or slovenly made drawings; that there were no more mix-ups with the manuscript is certainly no fault of such authors. This indifference of authors to their own papers caused an immense amount of extra work for the working staff and for the Committee on Papers and Publications and gave rise to a very large correspondence not only unpleasant but wholly avoidable by just a little forethought on the part of the authors, the necessity for which had repeatedly been brought to their attention. The Congress should have power and it should be thoroughly understood that the power would be rigorously exercised, to return and reject any such manuscript peremptorily. That seems to be the only way to make such useless work impossible.

3. No paper should be considered unless its author or authors be members of the Congress at the time the paper is received; all papers should be short and concise; otherwise the abstract only should be printed. It is doubtful if papers can be properly handled and printed, reprints provided and the volumes packed and addressed ready for forwarding for less than one membership fee for each printed page of text or illustration; if the expenses incident to propaganda and solicitation of papers are added, the cost per printed page of text or illustration will be very close to 1.5 membership fees or 0.67 page per member. At the Eighth Congress there were 4,163 members whose fees would have provided for the printing of a total of 2,776 pages, whereas the first twenty-four volumes alone contained 5,143 pages of printed matter; this amounts to 1.3 pages per member or twice each member's allotment; the total publication dealing with papers contains 6,500 pages or 1.5 pages per member or $2\frac{1}{4}$ times each member's allotment. There were 789 papers or an average of 8.2 pages per paper, *i. e.*, each paper used up 12.3 membership fees or 11.3 in addition to its own; the number of papers was 18.8 per cent. of the membership. It is clear that if the individual papers of the future are to be of the same average length, that for each paper submitted there will have to be no less than thirteen members of the Congress if these Congresses are to pay their own legitimate expenses. Maintaining the present membership fee, there are only two ways of avoiding this situation: increase the membership or cut down the number and length of papers. Judging from the experience of the Eighth Congress the latter is the only way feasible; 4,000 or thereabouts seems to be the limit of membership.

4. If the papers are to be printed in advance, then ninety days before the Congress meets, no further papers should be received and no further memberships nor delegations accepted. At the Eighth Congress 560 papers were received in time to be printed before the Congress met; 229 papers were received too late for such publication; there is no reason why all but a very, very few of these papers could not have been presented at the time the other 560 were; this procrastination of authors has caused a delay and an injustice to members and authors who

have complied with the reasonable requirements entirely out of all proportion to any gain therefrom; memberships and delegations can be determined upon and concluded ninety days before the meeting as well as at any other later time; last minute members are rarely desirable or welcome.

With this thoroughly understood by all, the Committee in charge could have all the papers printed in advance and ready for distribution to those members in attendance; directly after the close of the Congress the volumes then ready could be forwarded to those members not in attendance; the membership list and organization list would be complete and printed and made a part of those volumes; the program could be made up and printed and mailed to every member sixty days before the Congress meets and every author would know just when and where his paper would be up for discussion. The indexing work could be brought up to date and would merely need to have added to it the matter contained in the supplemental volumes, *i. e.*, discussions, general lectures, joint-session addresses, minutes of the last General Meeting, errata sheet and index.

Without some such definite agreement and understanding the Committee in charge will have its time and energies absorbed in attending to the late-comers and be practically forced to neglect or slight the work necessary to prepare properly for those who have been prompt: manifestly, an improper and wholly unjustifiable state of affairs, which most properly will cause dissatisfaction; but that dissatisfaction ought not be levelled at the Committee; the procrastinating and late-coming authors and members are the ones open to censure. The only means of avoiding such dissatisfaction is to have an understanding and to stick to it. A gathering of this kind cannot be successful through the work of the Committee in charge alone; members *must* cooperate in the manner laid down by that Committee and not try to run the meeting each in his own way as so many evidently attempt to do. Members owe a duty to the Committee quite as much as the Committee owes a duty to the members, and unless members cooperate with the Committee in the way the Committee suggests, confusion and dissatisfaction must surely result and the cause thereof lies with the members themselves. It is, of course, unpleasant to write this paragraph but events at the Eighth Congress fully warrant and justify these remarks, and they are here made in the hope that the unnecessary labors which the Committee in charge of the Ninth Congress may have to perform will thereby be much less than they otherwise would be.

5. The work performed by the Committee on Papers and Publications fully justifies the introduction of this check into the organization of these Congresses and should be retained. While it is true that the final selections of that Committee are not satisfactory to all nor thoroughly consistent, yet it is equally true that this Committee prevented much discreditable matter from being printed and given the prestige of the Congress. Papers of the rankest kind of advertising nature, of the most sophomoric and puerile character, of the most verbose quality and without point or conclusion were offered to and rejected by this Committee; elaborate papers on topics of limited or no interest to chemists, papers made up largely of matters as old as chemistry itself, without any modern application were among those rejected. Direct fraud, evasion and deception were attempted by a number of would-be contributors from whom such acts would not and could not be expected or believed, but were detected and frustrated; papers published early in 1912 were offered in June, 1912, in the hope that the Committee would not know of such publication; one author had persuaded a Sectional Committee to pass a ninety-three page printed book for publication, and this author had taken extreme care to obliterate from his submitted copies every trace that would throw any light on its

origin or date of publication; he overlooked, on one copy, to erase or deface the imprint of the printing house and through this the Committee located that publication and found it had been on the book-markets since 1909 and that its preface was written in October, 1908! These are merely a few of the discreditable acts on the part of would-be authors that this Committee blocked and frustrated. There were many other cases where misrepresentation, falsehood, subterfuge and equivocation were resorted to in unsuccessful attempts to have papers accepted. The conclusion seems irresistible that most of these would-be authors regarded the publications of this Congress as a convenient dumping-ground for papers not elsewhere desired—a thing which the Eighth Congress in no uncertain terms had declared that it was not. Of course, this Committee was powerless to prevent certain instances of bad faith on the part of authors of accepted manuscripts who published such accepted matter in journals in other countries between the date of acceptance and the meeting date of the Congress; there is probably no way of adequately reaching such persons. These are harsh statements, but they are true and no doubt will cause as much astonishment to others as the actual facts did to the Committee.

The constructive work of the Committee has not been as uniform nor as satisfactory as that Committee itself wished, but this is because no precedent was at hand except the vague one deducible from the nature of the papers printed by preceding Congresses and because wherever there was a doubt that doubt was resolved in favor of the author simply because of this vagueness; of course, the few guideposts to be found in the rules on papers and publications adopted by the Executive Committee of the Eighth Congress were followed but they did not cover very many cases. The problem of determining what papers should be received is a difficult one and a solution for it will probably not be readily found. Personally, I incline to the belief that no paper which does not show within itself, expressly stated, an application of its subject-matter to a going industrial operation should be accepted and then only if the subject-matter be new since the last Congress and not previously read or published elsewhere; this is offered as a first approximation toward a solution and not for any other purpose.

It must be clear, however, that a Committee which has to determine the nature of the material for which so heavy an expenditure as $1\frac{1}{2}$ membership fee per printed page is to be made, performs a necessary and useful function and is a Committee which should have for its guidance as distinct and definite a ruling as possible and power to follow that ruling regardless of consequences.

6. The difficulty with discussions is to get a printable record; many participants get up without knowing just what they want to say and make remarks which are too ephemeral for publication; others have something of more or less importance to say which may or may not be worth while perpetuating; to sift out the permanent from the ephemeral is the task of the Sectional Secretaries, and this cannot be done in the meeting itself; the safest way is to obtain from each participant a statement of his remarks and *then* the participant must be asked for help in editing or cutting down the reports. Now the hard, cold fact is that the average participant does not like to be called upon in that way; he is at the Congress for a holiday, with labor as a distinct side-issue; he wants to meet his old friends, to make new ones and to see the sights; he is altogether too busy enjoying himself to bother with writing out or checking up the transcript of his remarks. The Secretary may enclose the most pleading note with that transcript or may make the most dire and awful threats, but your average participant serenely pursues his way and leaves the Secretary to his troubles gladly making him a present of his own into the bargain while all the Secretary can do is grin and bear it and be blamed and criticized afterwards because such participant's remarks did not appear.

The only remedy seems to be to give the average participant a little breathing time by having sectional meetings on alternate days, say Monday, Wednesday and Friday from 10 to 12 and 1 to 3; this would give each section six meeting periods of two hours each or a total of twelve hours. With the papers printed in advance and the program made up and circulated sixty days in advance of the Congress the reading of papers would be reduced to a mere formality; the discussion thereof would be the only real business left for a sectional meeting. Aside from a few comprehensive but concise introductory remarks in which the debatable points or some of them are brought prominently forward, the author, if present, should not say anything before the discussion opens; at the close of the discussion the author should be given opportunity to answer criticisms or supply additional information. At the Eighth Congress about one-half of the papers presented were discussed; the average time used in reading a paper was eight and one-half minutes, in discussion the average time was twelve minutes per paper discussed. With the above mode of reading the papers, the average time for reading need not exceed two or three minutes; in eighteen minutes two papers could on the average be presented and discussed, that is, on the average one paper every nine or ten minutes or seventy-two in all to the section. Tuesday, Thursday and Saturday morning could be available to the "average participant" in editing the transcript of his remarks or in writing them out; he would be deprived of his stock excuse that he has to rush off to another sectional meeting and must not neglect his other duties to the Congress for such clerical work as he can do later on just as well. At the Eighth Congress the participants did not get their edited remarks to the Sectional Secretaries until weeks and weeks after the Congress adjourned, and it was almost six months before the last Sectional Secretary's report came into the Secretary's hands—all because of the shilly-shallying of the participants in discussion. Perhaps, with some such arrangement of the meetings the average participant could be pinned down to his work, so that the Sectional Secretaries could all have their work cleaned up within a week after the close of the Congress for it must not be forgotten that each Sectional Secretary like Mr. Average Participant wants to meet his old friends, make new ones and see the sights; also that the former is quite as much entitled to that relaxation as is the latter.

There should be a distinct and separate authoritative provision, widely published, that all participants in discussion who do not have the corrected report of their statements in the hands of the Sectional Secretaries within three working days after the close of the Congress shall forfeit all right to have their remarks printed and that this provision is to be rigorously enforced. In the last analysis, this is the only way in which such procrastinators can be reached. As things are now, the Secretary is criticized because he goes to press too soon by those lazy and indifferent persons and criticized for going to press too slowly by those who are not in attendance—an intolerable and wholly unnecessary condition.

7. Registration by sections should be abolished. At the Eighth Congress only 228 out of 1,883 or only 12 per cent. registered by sections, and at no sectional meeting was a list of registrants for that section called for, nor was there any occasion for its use.

8. At the Eighth Congress a suggestion, made to it in the very best of good faith and which on its face gave every promise of the very best results, was followed; namely, having existing foreign societies attend to all matters of the Congress within their own territory. This has not worked out as satisfactorily as the previous method of appointing one man or one society in each country as the organizer. "What is everybody's business is nobody's business" applies to this mode of procedure quite as well as to activities in other walks of life. Concentrate

the responsibility upon one man, or one organization in each country and the results will be far more satisfactory. In order to prove this for the Eighth Congress it is only necessary to compare the elaborate organizations in some countries and the results of their work in membership, papers or attendance with the less elaborate organizations and their results in other countries and to see that, in efficiency, the latter far outstripped the former; in promptness and despatch the latter also were far superior to the former.

9. Chemists should appreciate, no matter on what plan or lines future Congresses may be conducted, that attendance upon these meetings is not necessary in order that they themselves may get the worth of the membership fee. The Proceedings of these Congresses go forward automatically, when ready, to each subscribing member and these are worth to each member at least as much as, if not many times more than his fee. Chemists at large should appreciate that they are each contributing to these gatherings by subscribing, even if they do not attend and that memberships beyond those in attendance are needed and *absolutely necessary* to make these Congresses a success and independent of bounty or charity; in fact, such subscriptions are just as essential to the success of these meetings as is attendance or contribution to the papers or the discussions. But, in order that these non-attending members be not unjustly treated it is necessary that *all* members and *each* member *without exception* do his share promptly and in conformity with the suggestions of those in charge; otherwise, as in the Eighth Congress, the forwarding of the Proceedings to such non-attending members will be delayed to such an extent as to be virtually, though not intentionally, a matter of injustice to non-attending members who are each entitled to just as much consideration and courtesy as is any attending member. In the Eighth Congress, the Committee in charge was utterly powerless to prevent such a condition. If work is withheld from it, no Committee can proceed. It should be remembered that such a Committee is practically delivered into the hands of its lazy membership and such a Committee can move no faster, as a whole, than the slowest moving member of the Congress; each member must do the whole of his share and do it promptly. Had this been done by all members of the Eighth Congress there would have been literally hundreds of membership fees otherwise disbursed, now made available for constructive work for the Ninth Congress and the publications of the Congress would have been completed four months sooner than they actually were; the number of such lax members reaches an astounding and almost unbelievable total.

This brings me now to my final observation which is valid, however future Congresses may be operated and that is that a very large proportion of the attending members fail to realize that all the officers and committee members of a Congress are also members of that Congress; that the services of these officers and committee members are given gratuitously to the cause and that the relationship is not that of master and servant or employer and employee, nor of guest and host, but of colleague and colleague earnestly striving, each in his own field of responsibility, to make a success of a largely altruistic undertaking; that the very least the member can do is to ascertain the plan laid out and follow and live up to that with as little interference with the working of the organization provided as is possible. Further, the organization of such Congresses is temporary, its work is over in a few days and the greatest load is thrown upon it at the very outset; the staff is temporary, is not and cannot be familiar with all the routine (for the simple fact that no man can guess or state what that routine is surely to be), or know all the members and all the minute details of the business as can the organization of a bank, a railroad or similar large institution dealing year in and year out with a large number of the same details at once. If only a little forethought and the spirit of coöperation be exercised, matters must and will straighten

themselves out along the lines mapped out by those in charge. It is very easy to find fault and to criticize, but it is impossible to operate 2,000 or more different plans for accomplishing substantially the same thing at one and the same time, even though all these 2,000 or more plans singly, be equally good and as good as the plan decided upon.

All of the foregoing has been written in the hope and expectation that it will be of service; therefore no personal matters and no personal feeling, of both of which there is fortunately none on my part, appear therein. Some parts may be, and no doubt are, self-evident and obvious but it is the overlooking of the self-evident and the obvious that is the most common trait of men, inclusive, of course, of chemists; it is the self-evident and the obvious that so many fail to realize and consider; this oversight causes more delay and more disappointment than any other one thing and is the justification for bringing up here these self-evident and obvious facts.

The Ninth Congress received but little discretionary power at the last General Meeting of the Eighth Congress; all it has power to do is to determine the number and scope of sections and to alter their identification-numbers. In all other respects precedent would require it to proceed along lines similar to those followed by the preceding Congresses. Any change in policy must first be sanctioned by the International Commission of Congresses of Applied Chemistry whose President is Professor Paul I. Walden, President of the Ninth Congress. This Commission is not expected to take the initiative in any change of policy; the desire, if any, for such a change must come from the members of these Congresses themselves. The members of the Eighth Congress owe it to the members of the Ninth Congress to acquaint the International Commission of Congresses of Applied Chemistry with any desires they may have in respect to such changes.

90 WILLIAM STREET, NEW YORK

THE PRODUCTION OF SYNTHETIC AMMONIA¹

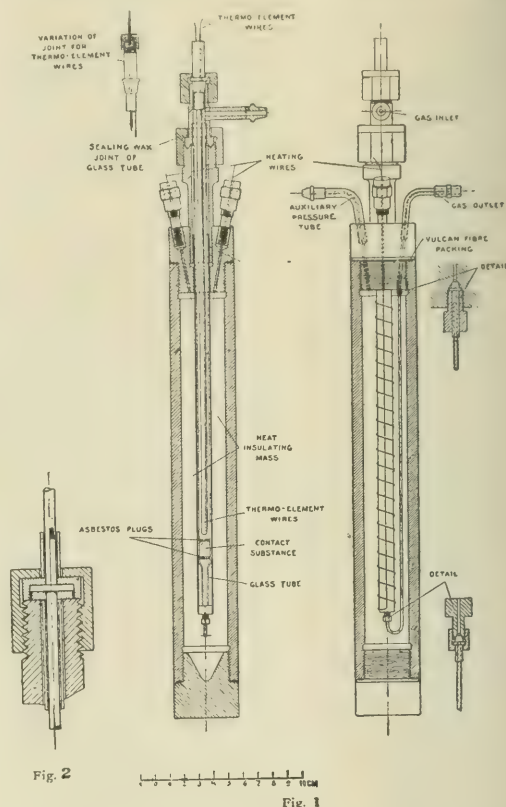
By F. HABER AND R. LE ROSSIGNOL

Ammonia in the form of commercial 25 per cent. ammonium sulfate possesses a value of 89 Pf. per kilo (9.5 cents per lb.), while the nitrogen and hydrogen of which it is composed may be valued at 2½ Pf. and 17½ Pf., respectively (2.14 cents for the nitrogen and hydrogen in 1 lb. of ammonia). The nitrogen is preferably obtained from air by liquefaction, as the resulting gas is relatively free from argon. It may also be made by the alternate action of air and producer gas on heated copper. Large quantities of nitrogen are generated as a by-product in the manufacture of formic acid from producer gas and caustic soda. The hydrogen may be obtained by the decomposition of distillation gases, by the alternate action of steam and reducing gases on iron, by the electrolysis of water, or by the action of water-gas on calcium hydroxide (*Ber.*, [1] 13, 719 (1880)). It is produced in large quantities also in the electrolytic manufacture of alkali and in the manufacture of oxalates from formates. The synthesis of ammonia from nitrogen and hydrogen depends upon the equilibrium represented by the expression:

$$K = \frac{p_{\text{NH}_3}}{p_{\text{N}_2}^{\frac{1}{2}} \cdot p_{\text{H}_2}^{\frac{3}{2}}}$$

where p represents the partial pressures of the respective gases and K is the reaction constant. Haber and van Oordt (*J. Soc. Chem. Ind.*, 1905, 131, 545) have studied this reaction, and found that at incipient red heat, equilibrium is attained when only traces of ammonia have been formed, and even under

increased pressure, which favors the formation of ammonia, the conditions are very unfavorable at incipient red heat or higher temperatures. The yield of ammonia corresponding to the condition of equilibrium increases as the temperature falls but the reaction velocity also falls off very rapidly. Haber and van Oordt's results (*loc. cit.*) indicated that in order to be able to work at atmospheric pressure, a temperature of about 300° C. must not be exceeded, but up to the present no catalyst has been found which is active at so low a temperature. The most active catalyst found by Haber and van Oordt was manganese, but the present authors have found osmium and uranium to be much more effective. The limits of temperature for prac-



tical working are between about 500° and 700° C. Above 700° C. any advantage accruing from increased reaction velocity is more than counterbalanced by the low yield of ammonia. At a little below 500° C. it is possible, at a pressure of 125 atmospheres, to obtain 0.5 gram of ammonia per hour per cc. of space in the contact chamber, and since in high-pressure work the size of the apparatus must be limited, it is not advisable to work at a lower temperature and hence with a lower reaction velocity. The results obtained are better the higher the pressure. Curves are given showing that at (1) 100 atmospheres and (2) 200 atmospheres pressure, respectively, the theoretical yields of ammonia at different temperatures are approximately: 500° C., (1) 10.7, (2) 18.1 per cent.; 550° C., (1) 7, (2) 12.2; 600° C., (1) 4.5, (2) 8.3; 650° C., (1) 3, (2) 5.8; 700° C., (1) 2.1, (2) 4.1 per cent. It will be seen that in no case is the yield so high that it would prove remunerative to absorb the ammonia from the reaction products, and allow the residue to go to waste. A continuous process must, therefore, be

¹ Abstracted by the *J. Soc. Chem. Ind.*, 32, 134 from the *Zeitschrift für Elektrochemie*, 19, 53 (1915).

adopted, the ammonia being removed and the residual gases, after addition of fresh nitrogen and hydrogen, being again passed over the contact substance. The simplest method of separating the ammonia is by liquefaction by cooling. Temperatures down to -75°C . may be used for this purpose, but below -75°C . there is risk of solidification of the ammonia, leading to stoppages. The regeneration of heat and cold in gas-liquefying apparatus with gases under high pressure has proved surprisingly efficient. However low the temperature, a certain fraction of the ammonia always remains in the gaseous condition and this fraction is somewhat higher than would be expected from the vapor-pressure table.

The apparatus used for comparing the efficiency of different catalyzers consisted, in its simplest form, of a strong steel cylinder with a bore of 6 or 7 mm. diameter, opening above into a conical enlargement into which fitted the conical lower portion of a steel cover. A special joint¹ was used here, and also wherever possible in the apparatus described subsequently, the conical portion of the cover having a more acute angle (16°) than the conical portion of the bore (20°); a hollow screw-threaded plug, fitting over a flange on the cover, was screwed on to the upper portion of the cylinder, thus bringing the two conical portions into effective contact. This apparatus was heated by means of a bath of fused saltpetre. Another form of apparatus (see Fig. 1) for comparing the efficiency of catalysts consisted essentially of a thin iron tube (0.6 mm. thick, 9–13 mm. diameter) wrapped in asbestos paper and wound with nickel wire (0.4 mm. thick) so that it could be heated electrically. The contact substance was contained between asbestos plugs in an inner quartz or glass tube sealed at the upper end, in which also was a quartz capillary, enclosing a thermocouple. The lower end of the tube containing the contact substance was flush with the end of the heated iron tube, and the latter was fastened by screwing and soldering to a steel capillary through which the gases were withdrawn. The whole was enclosed in an outer strong steel cylinder as shown. In order to prevent deformation of the heated iron tube by the high pressure, an auxiliary pressure tube was provided through which the gas mixture was introduced also into the space filled with heat-insulating material (asbestos paper) surrounding the tube. All joints in this apparatus were of the type described above, except in the case of the plugs closing the outer steel cylinder, and the insulated joints for the electrical heating wires. The joints of the steel cylinder were made gas-tight by means of discs of "Vulcan fiber," and the joints for the heating wires in the manner shown in Fig. 2, the wires being soldered to a small metal plate, about 2 mm. thick, which fitted into a recess in a disc of "Vulcan fiber" and was covered by another disc of "Vulcan fiber," both discs having central openings through which the wire passed. It is stated that in this furnace, with correct adjustment of the heating coil, a field of constant maximum temperature of 4–5 cm. length can be obtained. The largest furnace, which was used in the experiments with circulation of the gas, is shown in Fig. 3. In this furnace there is a heating coil in the gas space so that the mixture of nitrogen and hydrogen is heated before it reaches the contact substance, and cools gradually in passing over the latter; the formation of ammonia thus sets in at a relatively high temperature and hence with a high velocity, and further quantities of ammonia are formed during the gradual cooling, owing to the displacement of the equilibrium in a favorable direction. This furnace is also fitted with a heat regenerator, formed by a bundle of 127 steel capillaries, wound with iron wire, and supported by two hexagonal iron plates, perforated as shown in Fig. 3a, the capillaries passing through the perforations and projecting a short distance beyond the plate, which is provided with a rim. A powdered alloy of 40 per cent. of silver and 60 of copper is melted, with exclusion of air, around

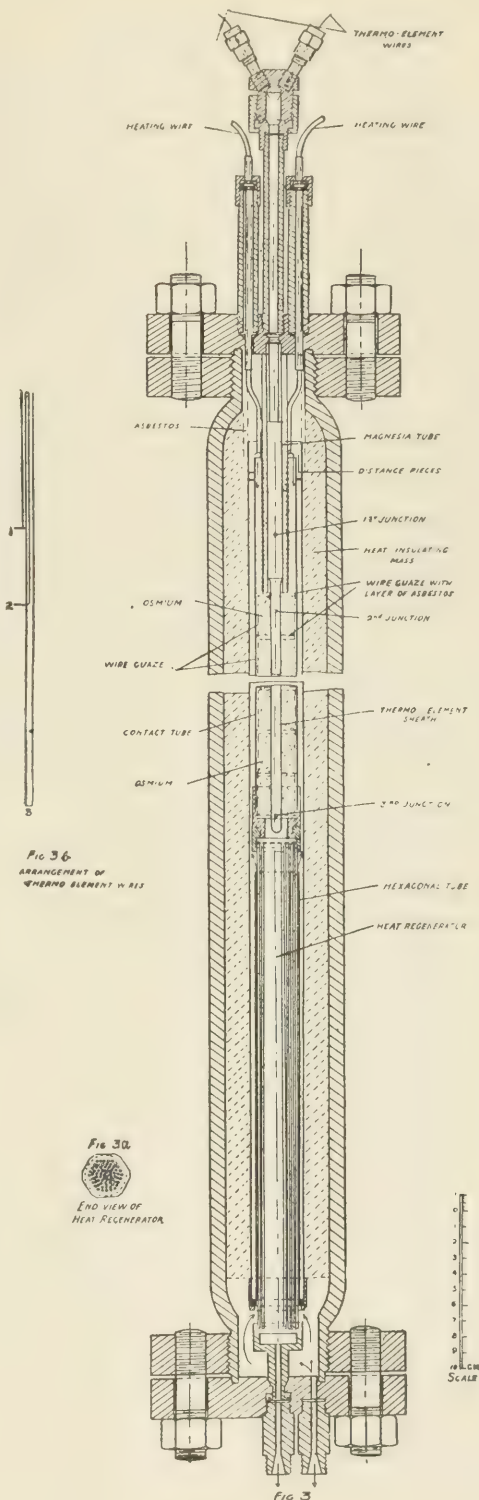


FIG. 36.
ARRANGEMENT OF
THERMO-ELEMENT WIRE

FIG. 3a.
END VIEW OF
HEAT REGENERATOR

FIG. 3

¹ D. R. G. M. 376,829 des Laboratoriums mechanikers F. Kirchenbauer.

the ends of the capillaries and fixes these in position. The bundle of tubes is enclosed in a hexagonal pipe. As shown in Fig. 3, the mixture of nitrogen and hydrogen entering at the bottom of the furnace, flows upwards through the hexagonal pipe, along the outer walls of the capillaries, then along the outside of the tube containing the contact mass, next downwards along the outside of the magnesia heating tube, and over the contact substance, and finally through the capillaries of the heat regenerator to the outlet. The magnesia heating tube is of 16 mm. outer and 9 mm. inner diameter and 15 cm. long, and is supported on an iron tube. Inside this is a thin iron tube extending down through the contact chamber and serving as a sheath for the thermo-element, which consists of a platinum-rhodium and three platinum wires arranged as shown in Fig. 3b. The length of the outer steel cylinder is 75 cm., the contact

layers of brass and cotton impregnated with paraffin, to a total length of 1.5 cm. At 300 revolutions per minute and a pressure of 200 atmospheres, the capacity of the pump was 72 cm. per hour (at atmospheric pressure and temperature), but the actual amount of gas circulated was somewhat less, owing to the leather packing of the piston proving not quite satisfactory; the stuffing-box packing answered very well. The ammoniacal gases from the furnace pass through a copper capillary to a drier charged with soda-lime and then to a heat-exchanger (cold regenerator) consisting of three copper capillaries united at the inlet and outlet; the capillaries are wound into coils as shown, and are contained in a strong steel cylinder. From the cold regenerator, the strongly cooled gas passes into the liquefier, and the liquefied ammonia is drawn off as necessary; or by opening the outlet valve to a suitable extent, the ammonia could be blown off as a uniform current of gas. The gases leaving the liquefier, pass through the cold regenerator to the pump, and thence again to the furnace, a fresh quantity of nitrogen and hydrogen being added on the way through a valve. Through another valve samples of gas could be withdrawn. For determining the ammonia content of the gas mixture, Rayleigh's gas interferometer as supplied by Zeiss was used, the gas being examined before and after passage through sulfuric acid (compare *J. Soc. Chem. Ind.*, 1906, 802). The results of experiments with cerium and allied metals, manganese, tungsten, uranium, ruthenium, and osmium as contact substances are described.

Uranium.—The commercial metal, broken up with a hammer, was used in a column of 4–5 mm. diameter and 3–3.5 cm. long. At about 600° C. vigorous formation of ammonia began. At 190 atmospheres pressure and the gas mixture flowing at a velocity of 20 liters per hour (measured at atmospheric temperature and pressure), the issuing gas contained 5.8 per cent. of ammonia constantly during 1½ hours. With a velocity of 3 liters per hour at 580° C., the ammonia content rose to above 7 per cent. and liquefaction of ammonia occurred at the valve. At a pressure of 120 atmospheres and a velocity of 3 liters per hour at 580° C., 4.8 per cent. of ammonia was obtained, falling to 3.5 per cent. on increasing the velocity to 20 liters per hour. With a velocity of 3 liters per hour at 550° C. (120 atm.), 5.6 per cent. of ammonia was obtained, rising to 5.85 per cent. on reducing the velocity to 2 liters per hour. Good results were also obtained with uranium prepared by Moissan's method.

An experiment extending over a long time with the commercial metal gave the results shown in the following table (p. 331).

The values marked with an asterisk were obtained not by determining the ammonia content at the given time with the interferometer, but by passing the gas during the interval between one test and the next through acid; they represent the yields corresponding to the mean of the values given in the same and in the succeeding horizontal series for the experimental conditions. It is important to heat up quite gradually in order to maintain the contact substance in an active condition. Experiments with uranium (pieces of the size of a pin-head) were also made in the simple steel cylinder, at a pressure of 125 kilos per sq. cm. With a velocity of about 32 liters per hour at 570° C., 5.65 per cent. of ammonia was obtained; 6.54 per

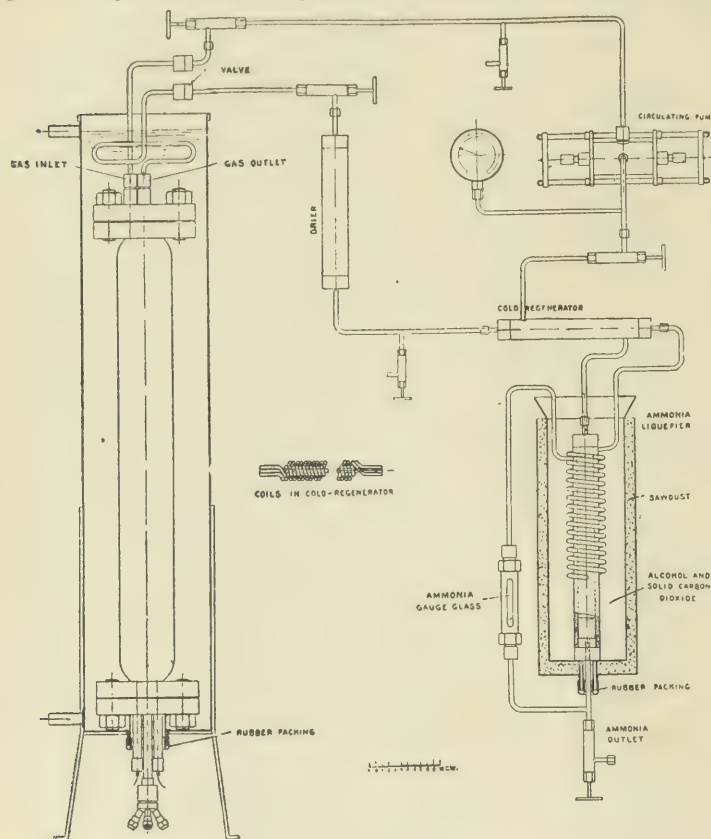


Fig. 4.

chamber is of 25 mm. diameter, and the tube enclosing the contact chamber and heat regenerator is of 32 mm. diameter; the space between the latter and the outer steel cylinder is filled with a stamped-in mixture of *magnesia usta* and finely-divided asbestos. The contact chamber was 25 cm. long and only a very small part of the space therein was actually filled by the contact substance. The covers of the outer steel cylinder were fastened by means of bolts, the joints being made tight by copper washers; the other joints were made as described before. In the experiments with circulation of the gas, the apparatus was arranged as shown in Fig. 4. A small double-acting steel pump was used, with a stroke of 3–6 cm. and a piston of 19 mm. diameter. The piston rods consisted of steel wire, 1–5 mm. diameter, and the stuffing-box packing consisted of alternate

Time Minutes	Temperature ° C.	Pressure Kilos. per sq. cm.	Velocity Liters per hour	Ammonia Per cent.
0	590	121	11	2.8
70	592	121	11	3.05
133	589	119	11	3.1
180	591	118	11	3.13
240	591	117	11	3.15
300	591	115.5	11	3.09
360	590	114	11	3.05
420	591	112.7	11	3.02
460	591	112	11	3.02
515	590	106	20	*2.85
613	594	157	20	*2.70
714	590	145	20	*2.50
823	(quite low at times)	131	20	*1.97
1093	ca. 590	118-115	20	*2.00
1118	590	156	20	2.68
1323	593	166	20	2.74
1333	590	165	10	3.60
1340	610	165	10	3.80
1348	609	164	20	3.00
1358	630	163	20	3.15
1365	608	162	3	5.05
1398	609	160	3	5.50
1428	590	158	3	5.50

cent. at 505° C., and 25.7 liters per hour; 9.1 per cent. at 496° C., and 9.5 liters per hour; and 11-11.9 per cent. at 503°-493° C., and 2 liters per hour.

Osmium.—Finely divided osmium proved a very effective catalyst. (In both the iron and chromium groups of metals, the metals of highest atomic weight possessed catalytic properties far superior to that of the metals of lower atomic weight.) In a series of experiments with a layer of osmium 14 mm. long and 4.5 mm. diameter, 4.75 per cent. of ammonia was obtained at 592° C. and 156 atmospheres pressure and a velocity of 20 liters per hour. At the same pressure, 5.91 per cent. was obtained at 572° C., and 10 liters per hour; 7.9 per cent. at 174 atmospheres, 550° C., and 1.5 liters per hour; and over 9 per cent. at 521° C., 174 atmospheres, and 1.5 liters per hour. In a prolonged experiment with a small quantity of osmium (a layer 4 mm. diam. and 1 cm. long), 34 grams of ammonia were obtained, and the contact substance was more active after 58 hours than after 3 hours. An experiment with gas circulation was carried out with osmium as catalyst. After pumping out air from the apparatus (see Fig. 4) the mixture of nitrogen and hydrogen was introduced up to a pressure of 185 atmospheres, and the circulating pump set working. A current was now sent through the heating wire (17-18 amperes at 56 volts). The temperatures registered by the three junctions of the thermo-element varied from 580°-635° C. at that next to the heat regenerator, from 750°-825° C. at the intermediate junction and from 880°-1000° C. at the first junction. At first the liquefier was not cooled, and the ammonia content of the gas-mixture rose to 5.4 per cent. The liquefier was then cooled with a mixture of alcohol and solid carbon dioxide and kept at -25° to -39° C., mostly -30° C. The experiment was continued for 4 hours, the pressure ranging from 193 to 163 atmospheres. The ammonia content of the gas varied from 2.4 to 3.1 per cent., mostly 2.6-2.9 per cent. (Higher figures would have been obtained with a larger quantity of contact substance.) About 500 cc. of liquefied ammonia (corresponding to 336 grams or 475 liters of gas at ordinary temperature and pressure) were obtained in the 4 hours. The heat- and cold-regenerators acted very efficiently. The copper capillary through which the gases left the furnace could be held comfortably in the hand quite close to the furnace. The cold regenerator had a thick coating of ice on the side where the gases entered from the liquefier, while on the other side it was at the ordinary temperature. At the end of the experiment the residual gas mixture contained 30 per cent. of nitrogen plus argon.

CHEAPER ALUMINA AND ALUMINUM FROM MINERAL SILICATES¹

BY ALFRED H. COWLES

If two briquettes be formed, one of kaolin (or clay) containing 19 parts of anhydrous pure clay and twenty-three and four tenths parts of salt; the other of 15 parts of charcoal to 100 parts of the first mixture; and these two briquettes, alike in size and form, be kept heated with water vapor in an oxidizing atmosphere at a temperature equal to or just above the vaporizing temperature of salt, it will be found that each briquette begins to be converted over its surface into a sodic-silico-aluminate which would have the formula of $(\text{Na}_2\text{O})_2(\text{SiO}_3)_2\text{Al}_2\text{O}_3$ if the clay and salt were pure. The vibrating gaseous molecules of watery vapor and oxygen bring about this change over all exposed surfaces of the two briquettes. However, this difference in conversion will be found: *the briquette containing no charcoal will require nine times as long for the conversion to penetrate to its center between walls, as the briquette containing charcoal.*

This result is not self-apparent, as the reaction requires an oxidizing atmosphere to oxidize the sodium produced before it volatilizes out of the briquette. That this result would occur was based upon hypothetical reasoning on my part, and its demonstration as a truth was brought about by experiments performed in the laboratory of The Electric Smelting & Aluminum Company at Lockport, New York. By coincidence, Dr. Adolf Kayser was my assistant in performing the experiments. Dr. Kayser in the early '90's attempted to develop this reaction commercially, using briquettes containing no charcoal in large kilns of a down-draft nature. The work had proved a failure as had also the work of William Gossage in 1862, and that of Gruneberg and Vorster about 1874-76. During these experiments, Dr. Kayser was of the opinion that they could not succeed because, as he thought they would produce reducing conditions. The experiments, however, proved that the conversion penetrated the briquettes nine times faster when charcoal was in them, than was the case when the briquettes contained no charcoal. This result taught that it was necessary to expose large surfaces or porous masses to bring about a rapid conversion. This could be effected in more than one way, but the problem of cooling the gases and simplifying the elimination of dust led to the adoption of a tunnel furnace of the Grondal type, with modifications to render it suitable for the process.

The fact that the reaction could be made to proceed rapidly, opened up an entirely new vista, one of assured success to the process. It meant that the volume of fuel gases and nitrogen necessary to pass through the charged furnace would become so far reduced as to permit of efficient commercial condensation of the hydrochloric acid evolved. It meant the employment of cheap fuel, sawdust, or charcoal made from sawdust with possible by-products from the same, and far greater capacity of output with the same cost of plant. It meant that the process could be applied to other aluminous materials such as potash feldspar mixed with chloride of potash or salt, securing the chemically equivalent reaction.

Dr. Kayser had evolved a method of opening or rendering leachable alkali-silico-aluminate containing sufficient alkali, which means nearly one molecule more than that which occurs in feldspar. This he did by heating to a sintering temperature two molecular weights of lime to each molecular weight of silica in said compound, after which the product may be leached and the alkali aluminate very effectively removed. Our company acquired this patent from him.

The process is easily understood. In the manner in which we are attempting to perfect it at Sewaren, New Jersey, in our present work, briquettes similar to those in Fig. 1 are formed

¹ Paper presented at the Joint Meeting of the American Electrochemical Society, American Chemical Society and Society of Chemical Industry, Chemists' Club, New York, February 1, 1913.

by the same clay working machinery that produces what is known as hollow ware or conduit bricks. When the clay, salt and sawdust are mixed together and water is added, this mixture acts almost the same as clay as to plasticity in passing through the briquetting machinery, but unlike the clay brick, it does not shrink or expand from the period of its first formation, during drying and until it is formed into a finished product containing soda, silica and alumina.

These briquettes are loaded onto flat cars, the surface of each car as now used being twelve feet long and five and a half feet wide holding fifty-five bricks. These loaded cars are passed first through a drying furnace where the free water is driven off, and then by a transfer track into a vestibule connected with the long kiln or furnace. After the door of the kiln is opened and the door of the vestibule is closed, the loaded car is gradually pushed into the charging end of the furnace by a hydraulic pusher, and a train of fourteen cars in front of it is also gradually pushed forward towards the discharging end of the furnace, while a finished car load is coming out at that end.

than that which takes place in the *reaction proper*. The amount of steam, if the heated zone in the furnace be long enough, can be so reduced as to still permit much water being admitted to the coke towers to complete the condensation of all the acid.

Above and on the end of the furnace where the cars are pushed in, is a large exhaust fan which draws all the gases from the furnace and forces them onward through a condensing system where the hydrochloric acid is condensed. The furnace is 184 feet long, or ignoring the vestibule, is 170 feet long. Beyond the zone of high temperature towards the fan, there is a distance of 79 feet where the briquette loaded cars act as scrubbers to remove any sublimed salt and other dust from the gases at the same time that the incoming briquettes are being heated by the hot gases passing over them.

In addition to this, we are constructing a dust settling and cooling chamber in the iron pipe line between the furnace and the acid condensing system.

The reaction that takes place in the furnace will vary according to the composition of the aluminous material and the amount

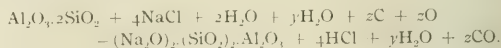


FIG. 1—BRIQUETTING MACHINE AND CARS WITH BRIQUETTES READY FOR FURNACE, SEWAREN, N. J. PLANT

The cars are covered with fire brick, the latter of a nature to protect them from being materially attacked by salt vapors. A sand seal extends the whole length of the furnace, and pure air is blown under the train of cars in such a manner as to prevent any leakage of hydrochloric acid fumes downward. In operation, the temperatures of all exposed iron parts of the furnace are kept above the boiling point of mixed acid and water, and as is well known, at this temperature vapor of hydrochloric acid does not attack iron.

Knowing the composition of the clay and the percentage of salt in the briquettes, steam is blown into the discharge end of the furnace, and the rate by pounds weight of steam per minute is read by an indicating steam flow meter. Suppose this rate is adjusted to the rate of feed of the material on the cars to effect the decomposition of salt with the formation of say 33 per cent. hydrochloric acid in water: then there is required in the *chemical reaction only about one part of water to 9.5 parts of water* to produce the 33 per cent. acid, hence it will be noted that the quantity of steam blown in to form such acid is 9.5 times greater

of alkali chloride mixed therewith, but typically it may be written as follows:



The gaseous products in the reaction are carried into the condensing system after cooling. The briquettes maintain their original form, and before the cars issue from the discharge end of the furnace they are cooled down by the inflow of the measured quantity of steam and air that is sucked in. This inflow becomes preheated by the hot bricks before it reaches the combustion zone of the furnace; the finished bricks are cool enough to be handled with gloves as they are discharged from the furnace.

In our work at Sewaren we have discovered that our acid condensing apparatus with air cooling has only about one-third the necessary capacity. It is at the present time being enlarged; also tourells submerged in water are being added into which about 18° Beaumé acid will be run against the flow

of the gases before they reach small coke towers. The escape of acid fumes has been so great that we have been able to make only four experimental runs of about thirty hours duration each with the large furnace, but the results secured have taught us the necessary changes to be made in the acid condenser system and those necessary to get a full conversion in the furnace. The whole product of the last two runs has been analyzed, but not of the first two. The furnace was operated with only one set of oil burners and a car of briquettes fed into the furnace every forty minutes.

Before starting to build our plant at Sewaren, briquettes had been made containing as high as 33 per cent. of sodic oxide and were white and free from iron.

We found by analysis that the Sewaren briquettes were but little more than half converted, hence it was rather against my desire to read this paper at this time. The briquettes still contain a large amount of salt. The furnace is provided with another set of oil burners to meet this contingency, but we have not yet used them.

After completing the enlargement of our acid condensing system we contemplate using both sets of oil burners and adding a trifle more sawdust to the bricks, in which case there is no doubt but that we shall produce the same results as in our

dust chamber completed, it will be practically free from salt and aluminum chloride.

LIME OPENING PROCESS

In order to secure from the sodic-silico-aluminate of the briquettes the sodic aluminate contained we intend to put down a kiln of the rotary type to sinter this material, which is easily friable after being mixed with lime in such proportions as to form dicalcium silicate from the silica present. This compound is insoluble, while the sodium aluminate is soluble. The material as thus treated is not fused, but sintered in such condition as to form an easily leachable mass. The reaction involved in this process is as follows:

$$(\text{Na}_2\text{O})_2 \cdot (\text{SiO}_2)_2 \cdot \text{Al}_2\text{O}_3 + 4\text{CaO} = 2(\text{CaO})_2 \cdot \text{SiO}_2 + (\text{Na}_2\text{O})_2 \cdot \text{Al}_2\text{O}_3$$

Limestone, calcite or marl in their chemical equivalents may be used instead of anhydrous lime. The product thus secured will be leached by ordinary methods.

In the foregoing reaction any amount over two molecular weights of calcium oxide to each molecular weight of silica leads to the formation of insoluble calcic aluminate, and less than two molecular weights leaves undecomposed a portion of the insoluble sodic-silico-aluminate. Under either of these contingencies, marked loss in the recovery of alumina may occur

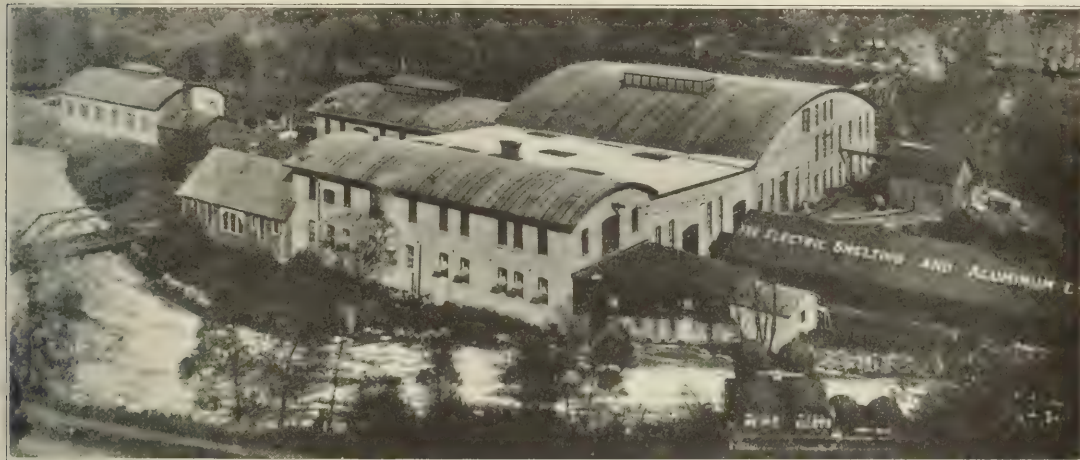


FIG. II. LOCKPORT, N. Y., PLANT OF ELECTRIC SMELTING AND ALUMINUM COMPANY

laboratory work, with one exception. In the laboratory work, the furnace was a deep circular one filled with briquettes and an oil flame and water vapor were passed downwards through the briquettes. Under these conditions, the iron as an impurity in the clay was carried downward as chloride of iron; small portions of it passed off with the acid and other portions condensed in the bottom of the furnace and in the iron pipes through which were drawn the gaseous product from the furnace from under a grate at its bottom. As these bricks were secured white it was concluded that we would secure the same result in our large work, but this conclusion as given in a paper¹ read before the 8th International Congress of Applied Chemistry, has, by practice, proved erroneous. Since the surfaces of the cars are cooler than the briquettes, we find a portion of the iron as either ferric or magnetic oxide on the car surfaces and a part still remains on the surface of the lower portions of the briquettes; hence it does not pass out with the gases to vitiate a part of the acid. The acid produced thus far shows the presence of sulfuric acid only by the most delicate test. It is free from arsenic, and has but traces of free chlorine, iron chloride, sulfuric acid, and ammonium chloride; with our final settling

Experimentally, up to 90 per cent. of the sodic aluminate has been leached from the above clinker while there was left behind a mass of dicalcium silicate.

PRODUCTION OF HYDRAULIC CEMENT

According to Newbury's formula, hydraulic cement is tri calcium silicate with up to 8 per cent. of aluminum and iron oxides in a mixed condition permissible. The above-mentioned dicalcium silicate product is hydrated. If it now be ground and then heated with one added molecular weight of lime it forms a product that is in composition the same as that of hydraulic cement, but unless the raw materials used are very pure, experience at Sewaren discloses that it will give a light gray and not a white cement as I believed when I spoke before the Eighth International Congress of Applied Chemistry. Inadvertently I also stated at that time as follows:

"When briquettes are made containing 32 per cent. of sodic oxide the output of 30 per cent. hydrochloric acid should be about one and a half tons of acid to one ton of salt and clay in the charge."

The statement should have read "To one ton of salt in the charge, about 1.75 tons of 33 per cent. acid."

¹ See Vol. 25, p. 119, also *Mt. Chem. Eng.*, 10, 659.

USE OF DICALCIUM SILICATE AS A MATERIAL FOR GLASS MAKING

If, in the foregoing lime sintering process, should 15 or 20 per cent. of the alumina and alkali contents left in the insoluble dicalcium silicate after leaching, there remains a product, that is excellent for the manufacture of window and bottle glasses. Its use would call for the addition of silica and more alkali. Glass can stand a considerable percentage of ferric oxide and alumina in its manufacture.

OXALIC ACID

Excepting sawdust nearly all the ingredients needed to produce oxalic acid come from the products of this process. The carbonic oxide from the acid towers can be scrubbed to free it from the last traces of hydrochloric acid and then passed over or through sawdust mixed with a caustic alkali heated to the proper temperature producing an oxalate of the alkali, which treated with calcium chloride gives calcium oxalate and with sulfuric acid gives oxalic acid with calcium sulfate precipitated. This acid is most largely manufactured in Europe, but has a great consumption in American laundries.

USE OF HYDROCHLORIC ACID IN PRODUCING PHOSPHATE FERTILIZER

The question may well be asked what use can be made of the large amount of hydrochloric acid that this process will produce should it supply as much alumina as will be needed for the production of the world's future supply of the metal aluminum. The author has pending a number of United States and foreign patents which may place hydrochloric acid in competition with sulfuric acid as now used in the manufacture of soluble forms of calcium phosphate mixed with calcium sulfate so largely used as a fertilizer. A pure calcium phosphate rock is anhydrous tricalcium phosphate. With it, there is almost always associated considerable calcium carbonate, silica, alumina and other impurities. If this rock be ground to an even degree of fineness and then thoroughly digested with weak hydrochloric acid, the quantity of acid employed being theoretically just sufficient to dissolve all the free calcium carbonate, ferric oxide and one molecular weight of calcium oxide contained in the tricalcium phosphate, the insoluble residue that is left is dicalcium phosphate. The soluble products—calcium, magnesium and iron chlorides—will exist in solution. By filtering and passing water through this mass, the soluble chlorides formed can easily be removed, and either run into the sea or submitted to other possible uses. The insoluble dicalcium phosphate remains in a non-hygroscopic pulverulent condition that can readily be applied to the soil by present methods of distribution. This is the product that all soluble phosphates revert to when they are applied to the soil as fertilizers. It has, however, one advantage over the soluble phosphates produced with sulfuric acid; *i. e.*, it is not loaded down with a large burden of calcium sulfate upon which transportation charges must be paid. If calcium sulfate is desired for fertilizer use, it can be more cheaply produced from native gypsum rock. If the digestion is not thorough, some soluble phosphates pass into the rich solution of chlorides. These phosphates can be precipitated by the use of a proper amount of calcium carbonate.

In Idaho, Utah, Montana and Wyoming, the U. S. Geological Survey has in recent years discovered and examined the largest deposits of phosphate-bearing rock ever known to the world. In this general region, those rocks that have now been withdrawn up to September 1, 1912, covered an area of nearly two million two hundred and twelve thousand acres.

The process as thus far described ends in securing the alumina as a sodic aluminate solution which can be completely purified from silica, titanate acid and the iron oxide by a very simple means of precipitation. The final precipitation of the alumina in its purest form is brought about by Dr. K. H. Bayer's process patented about 1894. It involves a very peculiar and inter-

esting phenomenon. When previously precipitated alumina is added to sodic aluminate solution, the precipitate begins to grow almost like a mushroom, and in a few days time nearly all of the alumina is precipitated, leaving a liquid containing nothing but caustic soda and a comparatively small amount of alumina. By an added step, which on account of patent matters I can not discuss, the last traces of alumina from the solution may be recovered, leaving a strong solution of caustic soda that needs slight concentration to prepare it for the market.

This general process opens the way to secure alumina cheaply or as a by-product in conjunction with these other products widely used in the industrial world. To produce one pound of aluminum 1.9 pounds of alumina are needed, there being no appreciable loss in the present method of manufacture of the metal. This weight of alumina costs from 6½ to 7½ cents according to the latest data and is the heaviest item of cost in producing the aluminum. By a general introduction of this process we may hope to see the cost of production of aluminum reduced 4 or 5 cents per pound. When it comes to a general electrification of our world's railroads and a greater use of electric transmission lines and trolley wires, we shall find aluminum a much more serious competitor of copper than at present; eventually, it will almost entirely supplant copper except in motors and generators.

POTASH ALUM FROM POTASH FELDSPAR AND ROCK PHOSPHATE

We all know the great need of potash salts as plant food and the scarcity of their supply, also the abundance of potash feldspar rocks containing great quantities of potash and the abundance of rock phosphate. Several years ago, I was experimenting with the mineral Wavellite which is a hydrated phosphate of aluminum. Knowing that calcium sulfate or burned gypsum is slightly soluble in water, and that aluminum sulfate is very soluble in water, I reasoned that if the proper proportions of aluminum phosphate and calcium sulfate were ground together and a minute amount of sulfuric acid were added to start the reaction, that the two bases should trade their acids if enough acid were present to form the insoluble calcium phosphate. On trying the experiment, I found this reaction to occur and that large amounts of aluminum sulfate could be leached away from the mixture.

Further, since dicalcium silicate is quite insoluble and calcium sulfate slightly soluble, it occurred to me that an intimate mixture of potash feldspar (*e. g.*, orthoclase, $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ or other potash silicates such as leucite) with the proper proportions of rock phosphate and sulfuric acid should give a system which would result in the formation of *insoluble* dicalcium silicate and *soluble* aluminum sulfate, potassium sulfate and orthophosphoric acid (H_3PO_4). Accordingly, I ground potash feldspar with rock phosphate (enough to furnish two molecular weights of lime to each molecular weight of silica in the feldspar), heated the mixture to a sintering temperature of about 1000° C. and leached with sulfuric acid; my first experiment gave almost 100 per cent. results.

For the purpose of this lecture, I have had the work repeated. In figuring the amount of sulfuric acid to use, my assistant took a little less acid than was used in the former work, and the result of the leaching has given a product containing all the potash and all the alumina from the feldspar, but only part of the phosphoric acid. Duplicate results have been secured substituting hydrochloric acid for sulfuric acid. The liquor in these two cases will give us either potash alum or a double chloride of aluminum and potassium associated with all the phosphoric acid contained in the rock phosphate employed. By this process, the dicalcium silicate or a slightly lower form of calcium silicate would be available for use in the manufacture of either cement or glass. Feldspar and rock phosphate can be secured very free from iron. The iron, however, follows the other products into solution. From either potash alum or the

double chloride of aluminum and potassium the chances of securing pure alumina are very favorable. Upon heating to a dull red heat, aluminum sulfate breaks down into alumina with liberations of sulfuric acid (SO_3) and the potassium sulfate can then be leached away. In the case of a double chloride of aluminum and potassium at a very low heat in the presence of the vapor of water, hydrochloric acid is given off with the formation of alumina; the chloride of potassium remains and can be leached away from the alumina.

To secure pure alumina from the above solution of chloride or sulfate salts with phosphoric acid is promising. The potash alum, however, cannot be separated by crystallization. By precipitation with sodic or potassic aluminate, if too much of either of these salts be not used, pure phosphate of aluminum may be secured.

POTASH PHOSPHATE FERTILIZER

In the foregoing, I have described the sintering at a comparatively low temperature of rock phosphate and potash silicates. I wish to call attention to the fact that this mixture is in some cases of greater fertilizer value than rock phosphate when used alone: for this use sinter and treat with the proper amount of sulfuric acid or of hydrochloric acid, if hygroscopic properties are not detrimental. By this new process the silica has taken the place of much acid that would be required, and the product is not loaded down with calcium sulfate, but instead, is loaded with potassium sulfate while the lime and silica is in such form as to be sufficiently soluble to furnish silica to plant food; further, the soluble lime is in a condition to act on the potash minerals in the soil displacing potash and thus rendering more potash available for plant food.

THE SERPEK PROCESS FOR THE MANUFACTURE OF ALUMINIUM NITRIDE¹

By J. W. RICHARDS

The production of aluminium nitride (AlN) on a commercial scale is proposed in the process of Ottokar Serpek, followed by the decomposition of the same by water or caustic soda solution, thereby liberating the nitrogen as ammonia and producing alkaline aluminate solution from which pure alumina can be obtained. This rather daring chemical proposition has directed attention to aluminium nitride, the conditions of its formation and its properties.

The existence of aluminium nitride was suspected for some time before it was isolated. A rather indefinite number of years ago, about 1890, the writer's attention was directed by his father to the fact that when metallic aluminium in a melted condition was skimmed and the skimmings or dross laid to one side, that on sprinkling water upon them these skimmings gave off an odor of ammonia. The only explanation which came then to be figured out for this phenomenon was that the hot aluminium in the skimmings oxidized to alumina, and that the rather high temperature thus produced locally caused the aluminium also to unite with the nitrogen of the air and form the nitride. In other words, that the aluminium united first with the oxygen and immediately thereafter also with the nitrogen of the air. On sprinkling these with water, the nitride would react according to the following reaction:



In the light of subsequent investigation and formation of aluminium nitride in other ways it appears that the explanation given in these early days was correct and that aluminium nitride is formed directly under such conditions from metallic aluminium and the nitrogen of the air.

Le Verrier, later, proved the presence of traces of nitrogen in commercial aluminium by dissolving it in caustic potash and

passing the nitrogen evolved into Nessler solution, and obtaining from it the ammonia reaction. He thus proved the presence of nitrogen in the metal and suspected it to occur as aluminium nitride dissolved in the excess of metal. In further experiments he treated aluminium with a current of nitrogen gas until it was saturated and noted that this produced considerable diminution in the tensile strength, elastic limit and elongation of the metal.

Prof. Mallet later obtained aluminium nitride corresponding closely to the formula AlN by heating metallic aluminium in a carbon crucible to a moderate temperature for several hours in contact with dry sodium carbonate. Some alumina is formed, some sodium vaporizes and some carbon is deposited; the reaction is probably as follows:



Aluminium nitride containing 34 per cent. nitrogen and 66 per cent. of aluminium was obtained as little, yellow crystals and amorphous drops. When calcined in the air it was found to lose nitrogen and form alumina; it is decomposed in moist air losing its transparency, becoming lighter yellow, evolving ammonia gas and finally leaving the alumina residue. Caustic potash solution and melted caustic potash both attack it actively, disengaging ammonia and forming potassium aluminate.

A later experimenter described the compound as a gray amorphous powder, but with properties otherwise similar to those described.

Coming now to the work of Serpek, we find his first proposition seemed to be the production of aluminium nitride from aluminium carbide, which is indeed a possible reaction. In his U. S. Patent, 867,615 (filed June 19, 1906, and issued October 8, 1907), he describes the passing of nitrogen or a gas containing nitrogen over aluminium carbide as an initial material heated to red heat. He describes the volume of the carbide increasing on being converted into nitride, and says that the absorption of nitrogen was increased by diluting the carbide with such materials as carbon or alumina or aluminium chloride; also that traces of hydrochloric acid or sulfur dioxide in the gas currents facilitated the conversion. The claims of this patent are essentially for the method of producing aluminium nitrides by heating aluminium carbide in an atmosphere containing nitrogen to a red heat with or without the diluting substances admixed and with or without traces of acid gas in the nitrogen used.

Attention may be called to the term "aluminium nitrides" in this patent, corresponding to the fact that in the product thus obtained by Serpek he found that part of the nitrogen in the product was driven off by contact with air, and a further part by boiling with water, and a still further part by treatment with caustic alkali solutions. These facts pointed to the non-homogeneity of the product, which thus appeared to consist of a mixture of different nitrides instead of one distinctive chemical compound.

Continuing his work we find that Serpek later concluded that it might be possible to obtain nitride directly from mixtures of alumina and carbon, which it will be recalled he used as diluent substances in the conversion of the carbide. He was apparently not able to produce nitride directly from these two substances, but found that in the presence of a small amount of a metal such as copper or iron, which is capable of forming an alloy with aluminium, the formation of nitride from the mixture took place. In his U. S. Patent, 888,044 (filed May 24, 1907, and issued May 19, 1908), he describes mixing alumina with carbon in the proportions necessary for the formation of CO gas ($\text{Al}_2\text{O}_3 + 3\text{C}$), adding about 5 per cent. of either copper or iron, or a mixture of the two, and heating the mixture to a red heat in a current of nitrogen gas, at which temperature the partial formation of an alloy of aluminium produced by reduction, with the copper or iron, would be initiated. The idea seems to have been to produce a mixture on the point of reaction from its

¹ Address presented at the Joint Meeting of the American Electrochemical Society, American Chemical Society and Society of Chemical Industry, Chemists' Club, New York, February 7, 1913.

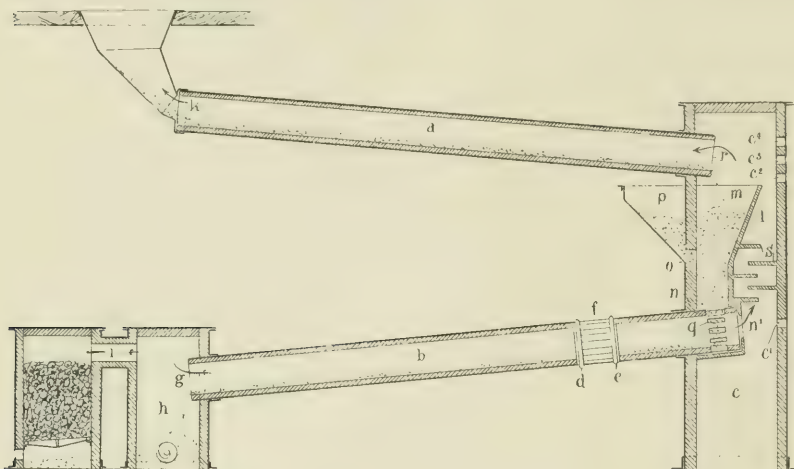
constituents and then to superadd the influence of the current of nitrogen gas. Traces of HCl or SO_2 gases are said to facilitate this reaction also, and the product is described as almost pure aluminium nitride. The reaction is said to develop a high temperature as soon as it is initiated. The claims are for producing aluminium nitrides by heating the mixture of alumina with carbon and a metal capable of forming an alloy with aluminium, to red heat in an atmosphere containing nitrogen, with or without the presence of small amounts of acid gases.

It is evident that in this method the conversion of alumina into aluminium nitride was aimed at, with the assistance of small amounts of metals as catalytic or assisting agents. Whatever may have been the results of the previously described process it led the investigator in the end to the method described in Serpek's U. S. Patent, 987,408 (filed December 15, 1909, and issued March 21, 1911), in which aluminium nitride is produced directly from Al_2O_3 and carbon in the presence of nitrogen, at a much higher temperature than previously recommended. This patent appears to be the result of considerable investigation on the conditions of this direct production and specifies very satisfactorily the temperatures at which the direct con-

verting alumina compounds and carbon, or more specifically alumina and carbon, in an atmosphere containing nitrogen to temperatures not exceeding $2000^\circ\text{C}.$ and preferably about $1800^\circ\text{C}.$

Reference may very properly be made at this point to the experimental investigation and confirmation of these results, by Prof. S. A. Tucker and Henry L. Read presented to the Eighth International Congress of Applied Chemistry and published in its transactions and in Volume 22, *Transactions of the American Electrochemical Society*. This investigation, carried on in the electrochemical laboratory of Columbia University under carefully regulated conditions, showed traces of nitrogen absorbed at temperatures of 1000 to 1100° and as much as 30 per cent. of nitrogen in selected portions of the product made between 1800 and 1900° . The product made at higher temperatures contained less nitrogen and was either sintered or fused. Impure alumina, such as bauxite, was found to be converted more easily than pure alumina, and the various statements of the Serpek patents were confirmed and verified.

Serpek's U. S. Patent, 996,032 (filed June 21, 1910, and issued June 20, 1911) contained a detailed description of the apparatus



SERPEK APPARATUS: *a*, upper calcining kiln; *b*, lower nitriding kiln; *c*, vertical connecting chamber; *c*₁, *c*₂, *c*₃, *c*₄, air inlets; *d*, *e*, electric resistance sectional heater connections; *f*, electrical resistors; *g*, inlet for producer gas; *h*, discharge of nitride product; *i*, exit for starch gases and inlet for ground bauxite; *l*, hopper for mixing calcined bauxite with carbon; *m*, calcined bauxite; *n*, ground carbon; *o*, mixing of carbon with bauxite; *p*, mixture descending to lower kiln; *q*, inlets to lower kiln; *r*, gas exit from lower kiln; *s*, baffle plates to promote partial combustion of gas; *t*, flame inlet to upper kiln.

version takes place. The patentee speaks of the general supposition that extremely high temperatures would be required for such direct conversion, such as the highest temperatures of the electric furnace, but explains that by careful investigation he had found that if the temperature is closely watched some combination of nitrogen with aluminium can be observed even at $1100^\circ\text{C}.$; that at 1500° nitrogen is absorbed fairly rapidly, at 1700° energetically, and that at 1800° to 1850° the reaction may be almost designated as violent, producing almost chemically pure nitride. Further, Serpek found that temperatures higher than this gave a smaller yield and that somewhere above 2000° the production practically ceased, the decomposition temperature of the nitride appearing to be about $2120^\circ\text{C}.$ This brilliant piece of experimental work really laid the foundation for the Serpek process as it now exists. The inventor further discovered that impure alumina, such as bauxite ore, was converted at somewhat lower temperatures than the pure material, evidently owing to the catalytic effect of the impurities present.

The claims of this patent are for producing aluminium nitride

intended for the commercial manufacture of the carbide from bauxite or other aluminium ores. The plant consists of two superposed rotating cylindrical kilns, similar in construction to cement clinking kilns. These kilns are inclined in opposite directions, so that the material being preheated in the upper kiln and passing from right to left, for instance, falls into the opening of the lower kiln for treatment at a higher temperature, where it passes from left to right. The bauxite alone is passed through the upper kiln, and there calcined, mixed with the necessary carbon in its passage from the upper to the lower kiln and the mixture treated by nitrogen at a high temperature in the lower kiln, which is provided with a detachable electric resistance furnace about midway of this length, intended to heat the charge within

to the reacting temperature, about 1800° to $1900^\circ\text{C}.$ The material is discharged from the lower end of this kiln into an air-tight receiver. A large gas producer of the ordinary type furnishes producer gas (approximately $\frac{1}{3}\text{CO}$, $\frac{2}{3}\text{N}_2$ nitrogen) to the lower end of the lower kiln. This gas entering at a temperature of about 400° , becomes highly heated as it passes through the kiln in a direction contrary to the descending charge, and at the electrically heated zone, at a temperature of 1800 to 1900° , reacts upon the mixture forming nitride. After leaving the high temperature zone the gas, enriched in CO coming from the reaction, preheats the descending charge, issues from the upper end of the kiln into a vertically closed chamber and passes through it to the opening of the upper kiln, where it meets a blast of air which burns it for the purpose of heating the contents of the upper or calcining kiln.

The apparatus as thus described achieves a methodical heating of the reacting mixture, utilizes the CO gas made in the producer and also that evolved by the reaction in the furnace; aims at an intimate mixture of the charge by the rotation of the cylinders, and intimate contact of the nitrogen with the charge.

The inventor states that the silica impurity of the ore is mostly volatilized (probably as reduced silicon) from the charge at the reacting temperature and is thus carried out in the gas; and that the apparatus may be used for producing other nitrides made by analogous reactions.

The claims cover an apparatus comprising the features of a revolving inclined upper cylinder discharging into an inclined lower cylinder revolving in the opposite direction, through a vertical chamber in which the gas from the lower cylinder may

be burned, combined with a detachable electric resistance heating furnace within the lower cylinder. One claim is for the single feature of a rotating calcining cylinder carrying a detachable electric resistance furnace.

Undoubtedly a large amount of excellent investigation has been put upon this process, and it deserves commercial success. The method is being tested upon a large experimental scale in France.

LEHIGH UNIVERSITY
SOUTH BETHLEHEM, PA.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

SULFUR MINING IN TEXAS

While the sulfur mining industry near Freeport, Texas, is, according to correspondence to *The American Fertilizer*, 38, 50, as yet more or less in a preliminary stage, the preparations which have been made for carrying it on and the claims which are set forth by the promoters of the new project, indicate that it may, perhaps, reach very large proportions. The sulfur deposits are owned by a syndicate of bankers and financiers, who also purpose carrying out the development, and the construction of a terminal system and port facilities.

Attention was attracted several years ago to the sulfur possibilities of the Freeport section of Texas, when several wells that were bored in search of oil upon Bryan Heights penetrated a deposit of sulfur at a depth of 700-900 feet. Systematic boring operations were then begun and these, it is said, demonstrated that the entire mound is underlaid by the sulfur deposit, "the available supply" from which "is practically unlimited." In December, 1912, the syndicate installed equipment upon the property, bringing the sulfur to the surface by the process in use in Calcasieu Parish, near Lake Charles, La. The mining equipment so far installed consists of a 6,000 horse-power boiler plant and the necessary pumping machinery for forcing steam into the well in operation.

NEW USES FOR NAPHTHALENE

The available annual supply of naphthalene may be thus expressed: Germany, 175,000 tons; England, 126,000 tons; France, 14,000 tons; and Belgium, 12,000 tons. Reference has already been made in *THIS JOURNAL*, 4, 308, to the use of naphthalene as an extraction agent; attention may be directed now to the use of an addition of naphthalene in the briquetting of bituminous coal (Grahn, *Gluckauf*, October 26, 1912) and to the employment of naphthalene as a fuel for explosion engines (Ventou-Duclaux, *Mem. Compl. rend. Trav., Soc. Ing. Civ.*, 65, 514, 598). The use of naphthalene in these connections is suggested by its low price and available supply.

When used as a fuel for explosion engines, special apparatus is necessary in order to obtain the explosive mixture of air and naphthalene, since the melting point of naphthalene (79° C.) is well above atmospheric temperature. Nevertheless, a number of advantages are gained thereby, viz.: (1) Low cost, which may be only \$0.0064 per horse-power hour; (2) security from fire; and (3) uniformity of composition. Naphthalene has been selected as the fuel for locomotives on the Trans-Siberian Railway.

NEW DEPARTURES IN ALUMINUM PLATE

An English concern which manufactures aluminum plate and vessels has had increasing success in introducing autogenously welded aluminum plate into various chemical industries. Reference has been made in *THIS JOURNAL* to the employment of aluminum in the brewing industry; it may be mentioned here that aluminum apparatus is now being used abroad

in the manufacture of essences and sirups, in varnish-making, in the fatty acid and edible oil trades, and in handling nitric acid. Aluminum storage tanks are said to be very appropriate for containing extracts, essences and essential oils; they are highly resistant to the acids contained therein, they are cheaper than copper, and they are light, clean, and unbreakable. Over 50 firms now use aluminum pots in the varnish-making industry (*Chem. Trade J.*, 52, 103); in addition to giving improved color, the metal itself is said to have proved highly resistant to the heat and action of the fire gases. "By using a thinner pot, a well-known Midland firm runs gums two shades paler than when using a standard thickness aluminum pot." An especially strong aluminum alloy has been introduced for making stirrers, in order to avoid the excessive abrasion of copper pots caused by steel stirrers. Aluminum has also proved itself to be durable under the conditions of high temperature, pressure and vacuum encountered in the fatty acid and edible oil trades, and it is said to result in freedom from taste and color; "besides its use for the neutral oils, aluminum has been adopted by some of the largest firms in the country for dealing with the fatty acids" (*Ibid.*). Welded aluminum tanks are now being employed for blending and measuring acids, as well as for piping for conveying the acid in the works; a number of aluminum tank cars have been constructed during 1912 for the conveyance of strong nitric acid in bulk, and the success of aluminum for this purpose is reported to be favorable, although only one such tank is now in service.

THE PAPER INDUSTRY OF NORWAY AND SWEDEN

A review of the pulp and paper markets in Norway and Sweden in 1912, which appears in the December 21, 1912, issue of *Farm- and*, contains the following statements regarding pulp production:

The production of sulfite cellulose in Norway and Sweden for export and for domestic consumption has been in recent years as follows, the figures being approximate estimates in tons of 2,000 lbs.:

1912, 992,079; 1911, 824,165; 1910, 809,096; 1909, 615,089; 1908, 686,739; 1907, 570,997; 1906, 440,924.

The production for 1913 is estimated at approximately 1,025,148 short tons.

The production of sulfate cellulose in the two countries was 188,495 short tons in 1911, and is estimated at about 203,927 short tons for 1912 and 212,746 short tons for 1913.

The most recent of the new sulfite mills, which were erected in the two countries as a result of the market conditions in 1908, has come into full operation during 1912 and will reach its full production in the course of 1913.

The increase in production for the year 1912 is estimated at about 149,914 short tons, but the estimates for 1913 indicate a further increase of only 33,069 short tons.

1912 STATISTICS FOR GERMANY

PIG IRON

The following table gives the total production of pig iron in

the German Empire during 1912, classified according to the purposes for which the iron was made and stated in metric tons:

	Metric tons	Per cent
Foundry iron	3,338,839	18.7
Forge iron	828,423	3.0
Steel pig	2,201,489	12.3
Bessemer pig	388,855	2.2
Thomas basic pig	11,397,965	63.8
Total production	17,852,571	100.0
Increase in production over 1911	2,298,541	

Steel pig includes spiegeleisen, ferromanganese, ferrosilicon, and all similar alloys. The largest proportional increase was in steel pig, which was 26.9 per cent. The iron ore imports for the twelve months ending December 31, 1912, were 12,120,090 metric tons; exports, 2,309,628 tons.

PETROLEUM

In 1912, Germany was supplied with petroleum by the following countries:

	Metric tons (1 ton is 7.6336 bbl.)
United States	769,468
Austria Hungary	156,267
Russia	34,939
Roumania	27,440
	988,414

POTASH SALTS

The sales of potash salts in 1912 amounted to \$42,142,857, as against \$38,819,047 in 1911. The exports of potash salts from the German Empire for 1912 were as follows, in metric tons:

	Total	To United States
Crude salts	1,300,529	650,297
Potassium chloride	286,528	190,775
Potassium sulfate	85,452	33,366
Potassium-magnesium sulfates	48,540	14,172
Total exports	1,721,079	890,610

GERMAN FOREIGN TRADE DURING 1912

The total imports during 1912 amounted to 71,399,926 metric tons, as against 68,409,628 tons in 1911; the exports were 65,490,111 tons as against 59,150,188 tons in 1911. The imports and exports of materials of importance to the chemical industries were as follows:

	Metric tons	
	Imports	Exports
Earths and rocks	4,152,655	4,190,218
Ores, slags and ashes	13,493,677	2,888,810
Fossil fuels(a)	18,441,913	39,854,657
Mineral oils and other fossil crude materials	1,815,729	109,953
Coal-tar, coal-tar oils, and coal-tar products	92,493	343,670
Prepared wax, solid fatty acids, paraffin and similar candle material, candles, etc.	47,873	41,534
Chemical raw materials, acids, salts, etc.	1,226,137	2,868,892
Pigments and pigment materials	78,289	241,531
Varnishes, lacquers, putty	3,111	6,298
Ether, alcohol, various essential oils, artificial perfumes, etc.	43,545	12,735
Artificial manures	519,246	969,715
Explosives and matches	685	21,270
Chemical and pharmaceutical products not specifically mentioned	63,292	46,081
Iron and iron alloys	673,910	6,020,902
Aluminum and aluminum alloys	18,227	6,225
Lead and its alloys	93,758	54,354
Zinc and its alloys	58,112	134,935
Tin and its alloys (including britannia metal)	15,712	9,538
Nickel and its alloys	2,142	2,528
Copper and its alloys	229,189	91,174

(a) The coal production of Germany in 1912 was as follows, in metric tons:

Coal	177,094,917
Brown coal	82,339,583

The coke made amounted to 29,141,070 tons and the briquettes to 24,391,701 tons; of the briquettes reported in 1912, there were 19,058,050 tons made of lignite or brown coal.

Of the more important materials, the imports of coal, artificial manures and explosives decreased during 1912 as compared with 1911. As to the other materials, the import figures show a variable but material increase, amounting in ores and slags alone to over 2 million metric tons. Except in the case of chemical raw materials, the export figures show an increase in all classes (*Chem. Ztg.*, 37, No. 12, 127).

POTASH FROM SEAWEED IN MEXICO

A concession has been granted to G. M. Bernstein, of Cananea, Mexico, to collect and utilize the kelp found floating along the western coast of Mexico, so far as relates to the entire coast of Baja. The principal plant is to be erected at San Diego. It is said (*Chem. Trade J.*, 52, 165) that one company has offered to take 400 tons of the kelp per day at \$5.00 per ton. This Mexican kelp has been rather a menace to shipping, for in many places it forms great islands, through which ordinary vessels find it difficult to sail.

A company has also been formed in Los Angeles, California, with a capital of \$1,500,000, to manufacture potash and other products from kelp. The new company is a consolidation of the Pacific Kelp Co. and the Coronado Chemical Co. It is planned to erect a large plant near Los Angeles.

POTASH FROM FELDSPAR

It is reported from Gothenburg that a Swedish engineer, Alex. Lindblad, is conducting experiments on the production of potash from feldspar. The mineral is electrically smelted along with coal and iron, and 100 tons of potash manure salts have been produced. It is planned to erect a large plant, but the economic manufacture will be dependent upon whether such large quantities of ferro-silicon as must be produced as a main product can find a market without depressing prices.

THE PRESENT STATUS OF THE THIOPEN PROCESS

The thiopen process for the removal of sulfur dioxide from smelter fume is based upon the reduction of the sulfur dioxide to elementary sulfur by means of fuel oil. When sulfur dioxide and a hydrocarbon of the ethylene series are heated together, the reaction which occurs is approximately as follows: $3\text{SO}_2 + 2\text{CH}_2 = 3\text{S} + 2\text{CO}_2 + 2\text{H}_2\text{O}$. Young (*Eng. Min. J.*, 95, 369) states that this reaction is, however, slow and incomplete, and that in order to obtain satisfactory results it is necessary to use some reagent as an intermediary. Such a reagent has been found in calcium sulfide. The reaction with calcium sulfide and sulfur dioxide may be represented thus: $2\text{CaS} + 3\text{SO}_2 = 2\text{CaSO}_3 + 3\text{S}$. The reaction occurs in the dry state fairly rapidly at 100°C , while in the presence of water it takes place readily at ordinary temperatures. If the mixture of sulfide and sulfur is heated, the free sulfur distills off and the residual calcium sulfite may be reduced at a moderate red heat by means of hydrocarbon oil, whereby the calcium sulfide is regenerated. The reduction is rather difficult except in the presence of iron compounds, but with small amounts of these, reduction takes place readily at a low red heat, and, very favorably for the process, the full reducing value of the oil is realized. The reaction involved is as follows: $2\text{CaSO}_3 + 2\text{CH}_2 = 2\text{CaS} + 2\text{CO}_2 + 2\text{H}_2\text{O}$. In practice, if a mixture of sulfur dioxide and hydrocarbon vapor pass together over a mixture of calcium sulfite and calcium sulfide, the reactions given above take place side by side; that is, a portion of the sulfite is attacked by hydrocarbons and reduced to sulfide, which is in turn attacked by sulfur dioxide and reconverted into sulfite, and so on. Thus the mixture of sulfide and sulfite serves the purpose of a contact material.

Experiments conducted at the Penn Smelter, Campo Seco, California, have eliminated many of the early difficulties encountered in the practical application of the thiopen process.

The present general scheme of operations in the process is as follows: The roaster gases pass first through a dust settler, which leaves them fairly clean, small amounts of dust seeming to produce no deleterious effect for a considerable time. From the dust chamber the gases pass to the fore-chamber, where a certain amount of oil is introduced. Thence the gases go to the contact chamber, where additional oil is introduced. The relative amounts introduced at the two places are adjusted by the temperature conditions which establish themselves in the contact chamber, the total amount being that necessary to burn out oxygen and reduce sulfur dioxide. The contact material is made up from plaster of Paris, which is mixed with water containing a small amount of iron salts, allowed to set and then broken into lumps. The issuing gases containing free sulfur pass to cooling and condensing apparatus, where the sulfur deposits. The principal chemical difficulties met have had to do with the poisoning of the contact material, owing to deposition of flue dust thereon, high temperatures, and the presence of foreign substances. The plant has been run for periods of 10 to 12 days upon the same charge of contact material, without loss of activity.

THE IODINE INDUSTRY

The ash of "tang" (sea-weed), which is now worked up for iodine in Norway, is shipped mainly to the iodine factories in England and Scotland. These factories, belonging to a trust, have depressed the price for sea-weed ash down to 2 cents per kilogram (a few years ago the price was still 3 cents); as a consequence, the calcination of sea-weed has diminished considerably in Norway. There are three small and unimportant iodine factories in Norway. The plan now is to erect a large modern iodine factory for working up 2,000 tons of sea-weed ash; this is intended to be entirely independent of the iodine trust, and is to be operated on a coöperative basis, in order to give the producers of the ash an opportunity to participate in the profits. It is also planned to manufacture norgine from sea-weed (norgine is a tungate of calcium, obtained by precipitating extracts from the sea-weed by milk of lime; it is used as an adhesive).

THE MANUFACTURE OF GAS MANTLES

Böhm, the author of "Das Gasglühlicht" (1905) and "Die Fabrikation der Glühkörper für Gasglühlicht" (1910), recently published (*J. Gas Ltg.*, 121, 33, 100, 181) a series of articles on the manufacture of mantles for incandescent gas lighting.

Cuprammonium-cellulose, Chardonnnet and viscose silks are all used for the manufacture of mantles; mantles of artificial silk combine the high and well-maintained illuminating power of ramie fiber with a great elasticity of the ash skeleton, and are now coming largely into use. Cotton mantles decrease in brilliancy after use, while those of ramie fiber are fairly constant. Cotton and ramie mantles must be washed before impregnation, in order to remove the fat and mineral matter, and to accomplish this the following process is employed: the mantles are soaked over night in a 2 per cent. solution of nitric acid, and the following morning they are centrifuged, treated with a dilute solution of ammonia, and then thoroughly washed. They are next dried in a current of hot air, any imperfect ones being removed. The mantles are impregnated by being soaked in a 25 to 33 per cent. water solution of thorium and cerium nitrates in the proportion of 99 : 1, to which very small quantities of beryllium and magnesium nitrates are added to harden and impart strength to the ash skeleton. The soaking period varies from one to two minutes in the case of ramie or cotton mantles, and requires five hours for artificial silk mantles. The superfluous liquid is removed by passage through a wringing machine, and the quantity of salts left in the mantles may be varied by adjusting the rollers of the machine. The mantles are next dried at a temperature not exceeding 30° C., for which purpose the cotton

and ramie mantles, which are cut into short lengths prior to impregnation, are stretched over glass cylinders, and the artificial silk mantles, which are impregnated in lengths, are run over wooden rollers. The upright mantles are next fitted with a sewn-on tulle head or with a patent head, and the latter is fixed by treating with a 50 per cent. water solution of aluminum and magnesium nitrates. The asbestos loop is next sewed on; the inverted mantles are drawn together with impregnated cotton, to form the "spider," and are then fastened on to the supporting ring. The mantle is shaped on a wooden shaper, and is then burned off by a Bunsen flame. The ash skeleton is dipped into a collodionizing solution, usually consisting of 100 parts of a 4 per cent. collodion solution, 40 parts of ethyl ether, 6.5 parts of camphor, and 3.5 parts of castor oil. After drying rapidly at 50–60° C., the mantles are trimmed to the right length, sorted out into different qualities, and the imperfect ones rejected.

ON SOME DEVELOPMENTS IN THE MINERAL OIL INDUSTRY

At a recent meeting of the Chemische Gesellschaft am Rigaschen Polytechnischen Institut, J. Hirsch presented a paper on the mineral oil industry, the following account of which appeared in *Chemiker-Zeitung*, 1913, No. 19, 198.

By means of modern rectification apparatus, benzines are now being obtained which boil within a range of less than 10° C.; the demand for benzines of low specific gravity has induced refiners in Europe to effect more satisfactory condensing arrangements; and, in Austria, the gases developed in winning petroleum are caught and condensed. Benzene products possessing a boiling point of between 130° and 180° C., and a flash-point of over 30° C. A.-P., are now finding use in varnish manufacture, replacing spirits of turpentine and rosin oil.

The burning oil industry of Europe has had much to contend with, for at the inception of the industry the lamps on the market were only suitable for burning American kerosene, and consequently there was much prejudice against the European product. However, by stronger heating and more abundant admission of air these complaints were remedied. It was also ascertained that the American oils could be duplicated by suitable methods of refining, by treatment at elevated temperatures with large amounts of sulfuric acid as monohydrate and with acids containing 20 per cent. anhydride. Treatment of the distillates with liquid sulfurous acid according to Edeleanu's patented process, was also found to be satisfactory. However, Hirsch states that it has been found that the cost of the products resulting from these methods of refining, is high. Experiments to replace caustic soda by caustic lime and to make the refining process a continuous one, have not met with success.

Hirsch states that the European petroleum industry is especially grateful to Ludwig Nobel for the introduction of methods of transportation (tank-wagons, tank-steamers, etc.), and to Victor Ragsin, who was the first to demonstrate the value of the residues for the manufacture of lubricants.

In producing lubricants from paraffin-free residues, decomposition must be carefully guarded against in the distillation; while, in the case of paraffin oils, a small amount of decomposition is desirable, for it accelerates the crystallization of the wax. The paraffin oils deposit the paraffin almost completely at 10° to 15° C. A preliminary separation of the crude paraffin is now conducted in filter presses constructed for a pressure up to 15 atmospheres. It has been found in Russian practice that the crude paraffin leaves the presses with a melting point of 44° C., as it contains 50 per cent. of oil. In freeing the wax from oil, it has been found that filter pressing according to the process of Nietsch and Winterstein, saves considerable time over the older methods of hydraulic-pressing and sweating. After refining the paraffin with acid and alkali, it is now bleached by treatment with "Hydrosilicate." Much progress has been

made in the construction of special machinery for the production and treatment of paraffin, and the author makes mention of some of the important European manufacturers.

THE WORLD'S PETROLEUM OUTPUT IN 1912

Petroleum Review notes that the world's petroleum production continues to increase, the 1912 output being as follows in barrels:

United States	219,000,000
Russia.....	63,000,000
Mexico.....	16,000,000
Dutch Indies.....	13,000,000
Roumania.....	12,500,000
Galicia.....	8,000,000
British India.....	7,500,000
Other countries.....	10,000,000
Total.....	349,000,000
Total in 1911.....	335,500,000

THE PROGRESS OF PAPERMAKING IN 1912

The report of Mr. A. D. Little to the American Paper and Pulp Association on the "Progress of Papermaking in 1912" appeared in *Paper*, 10, No. 11, 35.

The number of scientific papers bearing upon the paper and pulp industry which appeared during the year was only 127, and of these comparatively few had to do with important new developments or were otherwise notable.

Especially significant was the recent conference of over fifty paper manufacturers, representatives of testing laboratories, and others interested in paper specifications, which was called on January 24, by Dr. Stratton, of the Bureau of Standards, for the purpose of establishing a better understanding between the manufacturers and the Government officials who have the purchase of paper under their charge. It seems evident, Mr. Little observes, that the Government by the careful testing of deliveries furnished under its paper specifications has attained a two-fold result: First, a better and more uniform supply of paper; and, second, the protection of those manufacturers who have honestly endeavored to meet the specifications from the unfair competition of less conscientious bidders. Some progress was made at the conference toward greater uniformity of methods, and it was decided to hold similar meetings each year.

Further researches by Raitt into the papermaking qualities of bamboo amply confirm the general opinion of fiber experts to the effect that bamboo is particularly well adapted to the requirements of the industry and should become an important source of paper stock. Raitt concludes that the sulfate process is best adapted to the reduction of bamboo, and that 80 per cent. of the Indian bamboo stand is made up of species available for paper-making. He estimates that a mill producing 10,000 tons of bamboo pulp per year would require for a continuous supply of raw material a bamboo area of ten to twenty-two square miles.

Remington and others again called attention to the merits of Adansonia fiber as a stock for the manufacture of especially strong papers; the ultimate fibers resemble those of manila hemp. Von Possanner, after studying fibers from the German colonies, reports that *Ponzolzia hyppoleuca* yields 58 per cent. of unbleached fiber which is long and supple, and resembles, in some respects, both linen and cotton. Beadle and Stevens obtained results on treating *Heydchium coronarium* which indicate that this tropical plant has promising possibilities; the fiber is stated to be equal in strength to the best pure manila. The utilization of the pith and fiber of waste sugar cane, after extraction of the sugar, is being developed along altogether new lines by the United Fruit Company.

Notable examples of the utilization of waste material are to be found in the new mills of the West Virginia Pulp and Paper

Company at Covington, Va., for the manufacture of board of excellent quality from rossing waste; and at the mill of the Southern Wood Distillates and Fiber Company at Bogalusa, La., for the manufacture of board from waste wood by a new process involving treatment of the cooked waste under heavy crushing rollers.

The series of papers by Zacharias which appeared in sixteen numbers of *Papier-fabrikant* had, for their subject matter, the boiling and steaming processes for making brown mechanical wood pulp. These articles lead to the conclusion that boards made from boiled wood pulp show a decided advantage over steamed wood pulp board in tensile strength, resistance to folding, liability to tear, etc., and exhibit a greater stretch.

An important study into the causes of the yellow discoloration of paper has been made by Schoeller. Papers containing mechanical wood pulp discolor very readily with age, and papers containing straw and esparto are likewise subject to discoloration. Chemical wood pulp turns yellow to a less extent, while the paper made entirely from rags suffers slight discoloration. The coloring may be due to destruction of the ultramarine or other blue color used, or to actual yellowing of some component of paper. However, the most important cause of discoloration is the rosin size.

A RECORD OF INDUSTRIAL GROWTH

THE SEMI-CENTENNIAL OF THE FARBWERKE VORM. MEISTER LUCIUS & BRÜNING AT HÖCHST A/M, GERMANY

On January 4, 1913, the Farbwerte vorm. Meister Lucius & Brüning celebrated its semi-centennial. The history of this great firm is a record of the development of German chemical industry; the account which is given below is taken from *Die Chemische Industrie*, 36, 70.

In 1862, two chemists and two merchants organized a firm for the manufacture of tar colors, and the plant was started the following year with five workmen, one clerk, and one chemist. One boiler of 3 H. P. supplied the power. Fuchsin, anilin blue, alkali blue, aldehyde green, methyl violet, methyl green, and malachite green were the first products. In 1869, the manufacture of alizarine was taken up. In 1878, new buildings were erected for the manufacture of azo-dyes, and two years later the firm was formed into an Actien-Gesellschaft. In 1883, the manufacture of pharmaceutical preparations was started with antipyrine; in 1892, Koch's tuberculin and Behring's diphtheria serum were prepared and marketed; and in 1898 the manufacture of synthetic indigo was begun. The number of types of dyes and colors manufactured twenty-five years ago amounted to 1700-1800; to-day about 11,000 are manufactured. Salvarsan is another product of the concern.

In 1888, the steam engines had a total horse-power of 1840; to-day 30,000 H. P. are required.

The increase in personnel is shown in the following table:

	Year 1888	1912
Workmen.....	1860	7680
Foremen.....	50	374
Chemists.....	57	307
Engineers and other technical men.....	9	74
Office force, excluding agencies.....	86	611

In 1912, 8.6 million marks were paid in wages, and 5.2 million marks in salaries and bonuses. There is a pension fund, and benefit foundations have also been established.

THE LECITHIN AND ALBUMIN INDUSTRY

Lecithin became important industrially when Danilewsky discovered in 1895 that, when administered to growing animals, it was capable of stimulating their growth. It is now looked upon as the most valuable brain and nerve food yet discovered;

therefore, the discussion of its industrial aspects by Martin in *The Chemical World*, 2, 47, is of considerable interest.

The raw material for lecithin manufacture is yolk of egg, brain and nerve matter of freshly slaughtered animals, and seeds like peas and cereals generally. The bulk of the lecithin now on the market is made from yolk of eggs by extraction with solvents; by taking advantage of its different degrees of solubility in various solvents, it is possible to obtain it in a fairly pure state. Great care is, however, required, for being an unstable ester, incautious treatment rapidly hydrolyzes it into evil-tasting products. One process of recent development consists in extracting yolk of egg in the cold with ethyl acetate, whereby fats, cholesterol, coloring matters, etc., are dissolved out, and there remains an odorless, almost colorless mass, very rich in lecithin and albumin. This residue may then be directly used by being ground up, sweetened with lactose, and mixed with casein or wheat gluten or similar protein, and marketed in the form of tablets. When, however, pure lecithin is required, the mass is next extracted with hot ethyl acetate (sometimes boiling ethyl alcohol is employed), which dissolves out the lecithin, leaving behind the protein matter. Other worked methods consist in first extracting with alcohol, and then extracting the product dissolved by the alcohol with acetone, thus leaving the lecithin behind.

It is difficult to ascertain whether vegetable lecithin has been successfully placed on the market, but serious endeavors have been made to find a suitable process for extracting it from peas, cereals, etc. The demand for yolk of egg for lecithin manufacture has reacted upon the albumin industry.

230 to 290 eggs give 1 kg. of albumin, which is sold in thin, transparent leaves. In the manufacture of albumin, the evaporation is conducted *in vacuo* at 30-50° C. It meets with extensive application for photographic paper manufacture, as a constituent of adhesives and patent foods, as a fining agent, as a mordant in dyeing and calico printing, and, mixed with potassium dichromate, for preparing blocks, the mixture being sensitive to light.

Another variety of albumin is prepared from the blood of recently slaughtered animals. The albumin imported by Germany comes mostly from China.

(The grades of lecithin now on the market run about 70 per cent., 80 per cent., 90 per cent., and 95 per cent. "Lecith-albumin" contains 30 per cent. of lecithin; letalbin contains about 20 per cent. lecithin and 75 per cent. of albumin. "Lecithan" and "Lecithin Blattmann," said to be of vegetable source, are on the German market.—W. A. H.)

HOT WATER SUPPLY SYSTEMS TO MINIMIZE CORROSION

In a paper by F. N. Speller on the "Durability of Welded Steel Pipe," published in *Engineering News*, 1911, March 23, were discussed the results of investigations on the relative corrosion of iron and steel in service, and the influence of dissolved oxygen and carbon dioxide in water, and a scheme was proposed for rendering the water practically harmless by removing the air after heating.

Speller now reports (*Eng. News*, 69, No. 7, 295) that a recent investigation has developed interesting points in regard to the present practice of laying out hot-water supply systems. He states that the influence of the arrangement of the piping on corrosion seems to be quite marked, depending upon whether the gases are liberated before the water enters the distributing system or not, although the separation of these gases is only partially accomplished under the best conditions. In his investigations, only large installations were considered, where, on account of the great quantity of hot water used, serious trouble would be most likely to occur.

The hot-water supply systems found differ in many details,

but may be divided into two classes, according to whether the main vertical distributing lines are supplied from a common horizontal main in the basement, or from a similar horizontal distributing main above the level of the highest fixture near the roof. These types of installations are illustrated in Figs. 1 and 2.

The underfed system is characterized by a number of independent risers and return-risers, each supplying a separate section of the building. These risers are rarely vented at the top, and consequently the hot water is always supersaturated with air when the system is in continuous use. This is a good example of the closed type of heating so designed that it would be very difficult, if not entirely impracticable, to vent so as to remove the gases before the water is used.

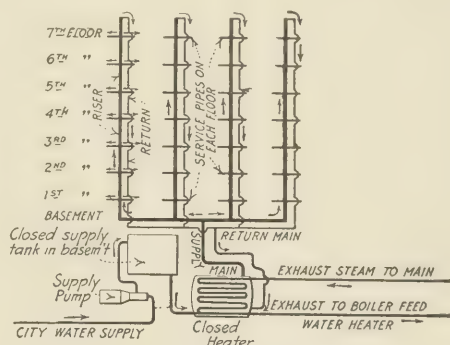


FIG. 1. UNDERFED CLOSED SYSTEM

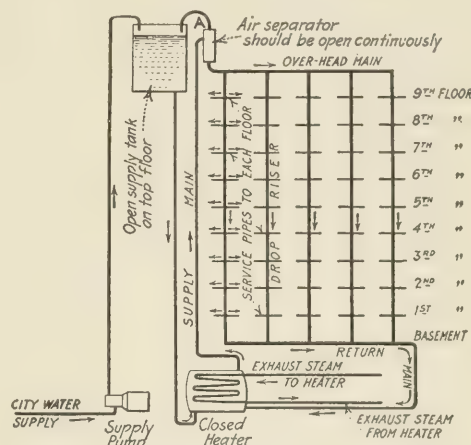


FIG. 2. OVERHEAD OPEN SYSTEM

The system illustrated by Fig. 2, on the other hand, is radically different in this respect, and to a considerable extent, although not completely, allows the escape of dissolved gases to the atmosphere at the highest point before the water is distributed throughout the system and returns to the heater. Since all the water used passes up through one riser, a vent must be provided, otherwise trouble due to the trapping of air in the upper lines would probably be experienced. It would seem to be a very simple matter to almost completely free the water from dissolved gases with such a system, by putting a simple air-separating device at the upper end of the main riser, as indicated at the point A in Fig. 2. To obtain the best results, the water

should be heated to about 200° F., using an inter-cooler, if desired, to reduce the temperature after leaving the air-separating chamber.

Several cases investigated, where large systems of hot water supply lines have suffered serious damage in six or eight years, have all occurred in buildings equipped with closed heating

systems. So far, Speller has not found serious trouble in systems of the open type where any attention has been given to venting, although the significance of adequate venting of such systems does not seem to be appreciated by engineers, for in some cases, where vents were provided, the practice was to keep them closed except when trouble with air-hammer was experienced.

SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY—FORTY-SEVENTH MEETING AT MILWAUKEE. PROGRAM OF PAPERS

GENERAL MEETING

Some Applications of the Hydrogen Electrode in Instruction, Analysis and Research. (Illustrated.) *Joel H. Hildebrand.*
Copper in Steel. The Influence on Corrosion. (Illustrated.) *D. M. Buck.*

Some Projection Experiments with Spectra. (Illustrated.) *H. E. Hesse.*

The Theory of Emulsions. *Wilder D. Bancroft.*

ILLUSTRATED PUBLIC LECTURE

Combustion. *Julius Stieglitz.*

DIVISION OF AGRICULTURAL AND FOOD CHEMISTRY

H. E. BARNARD, *Chairman*

GLEN F. MASON, *Secretary*

1. Chairman's Address. *H. E. Barnard.*
2. Studies upon Maize. *Carl L. Alsberg, F. Rabak, H. H. Bunzell and O. F. Black.*

3. The Equilibrium between Sugars and Sulfur Dioxide in Dried Fruit. *W. D. Bigelow.*

4. The Influence of Cooking on the Sulfurous Acid Content of Dried Fruit. *W. D. Bigelow.*

5. The Effect of Chicago Sewage on the Illinois River. *Edward Bartow.*
6. (a) The Composition of Canned Pumpkin. (b) The Tin Content of Canned Pumpkin. *H. E. Bishop.*

7. The Polarization of Light Colored Sugar Solutions. *A. Hugh Bryan.*

8. The Protein and Energy Requirements of Fattening Lambs as Determined by a Study of American Feeding Experiments. *Sleeter Bull and A. D. Emmett.*

9. Some Abnormal Factors of so-called Farmer's Cider Vinegars. *John C. Duggs.*

10. Analyses Showing the Composition of Different Grades of Commercial-pack Peas. *John C. Duggs.*

11. Methods for the Accurate Determination of Saltpetre. *J. T. Donald.*

12. The Modified Babcock Test for Fat in Sweetened Dairy Products—Ice Cream. *J. O. Halverson.*

13. Identification and Separation of Colors in Foods, with Particular Reference to the Permitted Colors. *P. W. Holtzendorff.*

14. Specific Heat Observations on Milk and Cream. *Arden R. Johnson and B. W. Hammar.*

15. A Thermal Method for the Determination of Ratio of Congealed to Uncongealed Moisture in Frozen Soils. *Arden R. Johnson and Roy E. Smith.*

16. Some Phases of National Food Control. *A. McGill.*

17. A Simple and Convenient Method for Determining the Salt Content of Butter. *A. E. Perkins.*

18. A Note Regarding an Absorption Tube and Receiver used in the Kjeldahl Nitrogen Determination. *A. E. Perkins.*

19. Organic Nitrogenous Compounds in Peat Soils. *C. S. Robinson.*

20. Some Chemical Changes taking Place during the Embryonic Development of the Chick. *R. H. Robinson.*

21. A Simple and Efficient 20° C. Bacteriological Incubator. *S. H. Ross.*

22. The Detection of Adulteration in Maple Syrup and Sugar. *J. F. Snell.*

23. A Comparative Study of the Composition of Hops Grown in Different Parts of the World. *H. V. Tatar and B. Pilkington.*

24. A Note on the Soluble Arsenic in Mixtures of Lead Arsenate and Soap. *H. V. Tatar and L. A. Bundy.*

25. Some Results of Hypochlorite Disinfection of the Baltimore City Water Supply. *J. Bosley Thomas and Edgar A. Sandman.*

26. Soil Acidity. *J. E. Harris.*

DIVISION OF BIOLOGICAL CHEMISTRY

CARL L. ALSBERG, *Chairman*

I. K. PHELPS, *Secretary*

1. Some Conditions Affecting the Stability and Activity of Certain Ferments. *J. H. Lono*

2. The Cholesterol and Cholesterol-esters of the Blood in Xanthoma Tuberosa Multiplex. *Jacob Rosenblum.*

3. A Chemical Examination of the Brain of a Syphilitic Foetus. *Jacob Rosenblum.*

4. A Problem in Metabolism. *W. D. Bancroft.*

5. The Development of Fat in the Black Walnut (*Juglans Nigra*). *F. M. McClenahan.*

6. A Study of the Renal Output of Rabbits Dying from Cottonseed Meal Poisoning. *W. A. Withers and J. F. Brewster.*

7. Certain Changes in the Nitrogen Ratios in Trout Eggs during Embryonic Growth. A Contribution to the Study of the Origin of the Energy of Development. *R. A. Gortner.*

8. Nephelometric Determinations of Proteins. I. Casein and Globulin in Milk. *P. A. Kober.*

9. A Laboratory Study of Well Water as a Cause of Typhoid Fever. *G. O. Higley.*

10. Influence of Cane Sugar on the Production of Tannase by *Aspergillus Niger*. *L. Knudson.*

11. Molds as a Factor in the Formation of Certain Nitrogenous Organic Soil Constituents. *M. X. Sullivan.*

12. Effect of Salicylic Aldehyde as a Soil Constituent. *J. J. Skinner.*
13. A Comparative Study of the Metabolism of *Pneumococcus*, *Streptococcus*, *Bacillus Lactis Erythrogenes*, and *Bacillus Anthracoides*. *M. L. Foster.*

14. A Biochemical Interpretation of the Inheritance of Acquired Characters. *L. W. Feltzer.*

15. The Chemical Effects of Ultraviolet Light on Albumin. *W. T. Bowie.*

16. Plant Growth in Relation to Acid and Alkaline Solutions. *Alfred Dachnowski.*

17. The Chemical Basis of Anesthesia and Irritability. *A. P. Mathews.*

18. Note on the Volatilization of Sulfuric Acid when Used as a Drying Agent in High Vacuum. (Lantern.) *H. C. Gore.*

19. A Constant Temperature Humidor. (Lantern.) *H. C. Gore.*

20. Study of the Chemical Changes in the Banana during Ripening with Special Reference to the Transfer of Water from Peel to Pulp. (Lantern.) *H. C. Gore.*

21. Study of the Effect of Uranyl Acetate and Ammonium Molybdate on the Polarization of *l*-Malic and *d*-Tartaric Acids. (Lantern.) *H. C. Gore.*

22. Cleavage of Hippuric Acid by Molds. *Arthur W. Dox and Ray E. Neidig.*

23. Bacterial Activities and the Rotation of Crops. *P. E. Brown.*

24. Purification of the Esterase from Pig's Liver. *George Peirce.*

25. Determination of Sulfur Dioxide in the Air. *Robert E. Swain and J. P. Mitchell.*

26. The Methyl and Methylene Ethers and Phenols Found in the Vegetable Kingdom and Light which They Seem to Throw on Certain Phases of Plant Metabolism. *Edward Kremers.*

27. The Analogy between the Formation of "Eyes" in Emmental Cheese and Crystal Growth. *W. M. Clark.*

28. Chemiluminescent Reactions with Physiologic Substances. *F. A. McDermott.*

29. A Note on "Oil Nut" (*Pyrularia Pubera*). *F. A. McDermott.*

30. On the Absorption of Water by Egg Yolk from Egg Albumen. *O. Riddle.*

DIVISION OF FERTILIZER CHEMISTRY

PAUL RUDNICK, *Chairman*

J. E. BRECKENRIDGE, *Secretary*

1. A Simple Method of Preparing Neutral Ammonium Citrate Solution. *Andrew J. Patten.*

2. A Survey of the Menhaden Industry. *J. W. Turrentine.*

Report of Committees:

Committee on Nitrogen. *Paul Rudnick.*

Committee on Phosphoric Acid. *G. A. Farnham.*

Committee on Potash. *J. E. Breckenridge.*

Committee on Phosphate Rock. *F. B. Carpenter.*

Committee on Fertilizer Legislation. *F. B. Carpenter.*

DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS

G. D. ROSENGARTEN, *Chairman*

1. The Training of the Fermentologist. *Carl A. Nowak.*
2. The Training of the Technical Chemist. *John Samuel Staudt.*
3. The Determination of Zinc in Treated Ties. *Francis C. Frary and M. Gordin Mastin.*
4. Preliminary Report upon a Practical Accelerated Test for Paints and Varnishes. (Lantern.) *A. M. Muckenfuss.*
5. Coal Ash. *S. W. Parr.*
6. Analyses of Glucose and Starch Sugars. *Edward Gudeman.*
7. The Specific Heat of Coal and its Relation to the Presence of Combined Water in the Coal Substance. *Horace C. Porter and Guy B. Taylor.*
8. Concrete Analysis. *Otto M. Smith.*
9. Fuller's Earth—Its Occurrence, Mining, Preparation, Use and Recovery. *Charles L. Parsons.*
10. The Uranium, Vanadium and Radium Situation. *Charles L. Parsons.*
11. A Simple Gasoline Gas Generator for Sulfur Determinations. *C. E. Waters.*
12. The Determination of Sulfate in Ammonium Sulfate with Special Reference to the Determination of Sulfur in Illuminating Gas. *R. S. McBride and E. R. Weaver.*
13. Determination of Sulfur in Illuminating Gas. *R. S. McBride and E. R. Weaver.*

DIVISION OF ORGANIC CHEMISTRY

TREAT B. JOHNSON, *Chairman*WILLIAM J. HALE, *Vice-Chairman and Secretary*

1. The Action of Cyanimido Ether on Esters of Amido Acids. *Lloyd M. Burghart and Ralph H. McKee.*
2. Zygadenine—The Crystalline Alkaloid of Zygadenus Intermedius. *F. W. Heyl, F. E. Hepner and S. K. Loy.*
3. Some Constituents in the Leaves of Zygadenus Intermedius. *F. W. Heyl and F. E. Hepner.*
4. The Rearrangements of N-Acyl Aromatic Amines. *C. G. Derick.*
5. The Efficiency of the Preparation of Ether from Alcohol and Sulfuric Acid. *P. N. Evans and Lena M. Sutton.*
6. The Constitution of Surinamine. *Ben H. Nicolet and Treat B. Johnson.*
7. A New Method of Synthesizing β -Ketone Esters. *Treat B. Johnson.*
8. Pyrimidine Nucleosides. *Lewis H. Chernoff and Treat B. Johnson.*
9. New Thiohydantoin Condensation Products. *Robert Bengis and Treat B. Johnson.*
10. The Constitution of "Acetylactone-Urea." *William J. Hale.*
11. Isodihydroaminocampolytic Acid and its Decomposition with Nitrous Acid. *L. F. Nickell and W. A. Noyes.*
12. Are Ammonium Compounds Atomic or Molecular? *R. S. Potter and W. A. Noyes.*
13. A Crystalline Resin Acid from the Digger's Pine. *O. A. Beath and Edward Kremers.*
14. The Oxidation of Indigo Blue by Phellandrene "Peroxide." *C. D. Geidel and Edward Kremers.*
15. Direct Halogen Substitution as a Laboratory Experiment in Organic Chemistry. *Edward Kremers.*
16. 2. Researches on Purines. On 2-Methylmercapto-6,8-Dioxypurine; 2-Methylmercapto-6-Oxy-8-Aminopurine. *Carl O. Johns and Emil J. Baumann.*
17. 1. Researches on Purines. On 2-Thio-6,8-Dioxypurine, 2,8-Dithio-6-Oxypurine; A New Method of Preparing Xanthine and Uric Acid. *Carl O. Johns and Albert G. Hogan.*

DIVISION OF PHARMACEUTICAL CHEMISTRY

B. L. MURRAY, *Chairman*P. R. ELDRED, *Secretary*

1. Observations upon the Assay of Digestive Ferments. (Second Paper.) *H. T. Graber.*
2. Blood Fibrin in the Assay of Pepsin. *A. Zimmerman.*
3. Some New Reactions of Peptones and Enzymes. *Fred Klein.*
4. The United States Pharmacopoeia; Progress of the Ninth Revision. *Jos. P. Remington.*
5. The Analysis of Thymol Capsules. *Atherton Seidell.*
6. The Riegler Method for the Determination of Thymol. *Atherton Seidell.*
7. The Interpretation of U. S. P. Assay Processes. *Frank O. Taylor.*
8. Patent Medicine Ethics. *W. D. McAbee.*
9. Ergot. *W. A. Pearson.*
10. The Recovery of Alkaloids when Precipitated by Alkaloidal Reagents. *L. E. Sayre.*
11. Oxyulphobenzid. *F. P. Summers.*
12. An Alkaloid from Peumus Boldus. *F. P. Summers.*
13. The Alkaloidal Content of Individual Plants of Datura Stramonium D. Tatula and other Species and Varieties. *F. A. Miller and J. W. Meader.*

14. A Study of American Grown Belladonna. *F. A. Miller and R. N. Reed.*
15. The Stability of Tinctures and Fluid Extracts of Belladonna. *R. N. Reed and W. J. Rice.*
16. Improvements in Mercury Gas-Regulators. *A. B. Davis.*
17. Prevention of Emulsification in Extractions by Immiscible Solvents. (Second Paper.) *G. H. Meeker and E. L. Maines.*
18. An Automatic Apparatus for the U. S. P. Pepsin Test. *Frank R. Eldred.*
19. Crystalline Periodides of Antipyrine. *W. O. Emery and S. Palkin.*
20. Laboratory Studies on Malt Extract. *H. T. Graber.*
21. The Determination of Uncombined Hydrochloric Acid in Ferric Chloride Solution. *C. H. Briggs.*
22. An Oleoresin of Pseudotsuga Taxifolia (Lam.) Britton. *O. A. Beath and Edward Kremers.*
23. Some Aspects of Pharmacopoeial Revision. *Edward Kremers.*

DIVISION OF PHYSICAL AND INORGANIC CHEMISTRY

S. L. BIGELOW, *Chairman*R. C. WELLS, *Secretary*

1. Some Surface Tension Phenomena. *S. L. Bigelow.*
2. The Oxygen Content of the Atmosphere. *O. F. Tower.*
3. The Role of Adsorption in the Catalysis of the Decomposition of Hydrogen Peroxide by Colloidal Platinum. *D. A. MacInnes.*
4. Detection of Cyanides in the Presence of Ferro-, Ferri-, and Sulfo-Cyanides. *O. L. Barnebey.*
5. A Method for Determining the Number of Valences in Molecules. *Albert P. Mathews.*
6. Various Reagents which Prevent the Action of Hydrochloric Acid on Permanganate in the Iron Titration. *O. L. Barnebey.*
7. Some New Ammonio Salts. *Edward C. Franklin.*
8. The Alpha-ray Activity of a Layer of Radioactive Solid as a Function of its Thickness. *Herbert N. McCoy.*
9. The Periods of Transformation of Uranium and Thorium. *Herbert N. McCoy.*
10. A Theory of the Origin and Continuance of Optical Activity in Nature without the Assumption of an Asymmetric Form of Energy or "Vital Force." *Arden R. Johnson.*
11. Atomic Weight of Yttrium. *James E. Egan and Clarence W. Balke.*
12. The Intergranular Cement in Metals. *W. E. Ruder.*
13. The Intermediate Ion Hypotheses and the Solubility of Salts of Higher Types. (Lantern.) *William D. Harkins, H. M. Paine and R. D. Mullinix.*
14. The Significance of the Exponent in Storch's Equation. *Stuart J. Bates.*
15. The Calculation of the Equivalent Conductance at Infinite Dilution. *Stuart J. Bates.*
16. Electrostenolysis. *Harry N. Holmes.*
17. Design for Specific Heat Apparatus (Electrothermal). *Arden R. Johnson and B. W. Hammar.*
18. The Relation of Geochemistry to a Proposed Basis for a Standard Potable Water. *Dr. J. Culver Hartzell.*
19. The Teaching of Quantitative Analysis. *E. H. Archibald.*
20. The Structure of the Trinitride Radical. *J. W. Turrentine.*
21. Demonstration of the Zeiss Gas Interferometer for the Estimation of Minute Traces of Gases. *R. H. Brownlee and R. H. Uhlinger.*
22. The Constitution of Certain Liquid Almagams. *Joel H. Hildebrand.*
23. The Precipitation of Gold by Manganous Salts. *Albert D. Brokaw.*
24. Tetraavalent (?) Nitrogen and Divalent (?) Chlorine. *Hans Mannhardt.*
25. On the Reaction of Sulfur with Potassium Hydroxide in Aqueous Solution. *H. V. Tartar.*
26. Binary Systems. (1) Hydrazine Ammonia. (2) Ammonium Trinitride Ammonia. (3) Ammonium Bromide Ammonia. *Frits Friedrichs.*
27. Sulfates of Yttrium. *Charles James and E. H. Holden.*
28. Nitro-nitrogen Trichloride and Electrometer of Ammono-Nitrogen Trichloride. Preliminary communication. *W. A. Noyes.*

SECTION OF INDIA RUBBER CHEMISTRY

D. A. CUTLER, *Chairman*DORRIS WHIFFLE, *Secretary*

1. Wild Lettuce Rubber. *Charles P. Fox.*
 2. An Adopted Wiley Extractor for Rubber Extractions. *Charles P. Fox.*
 3. The Sampling of Rubber Goods. *John B. Tuttle.*
 4. Preliminary Note on a New Method for the Direct Determination of Rubber. *L. G. Wesson.*
- Committee Reports and General Conference.
Secretary's report. Report of the Rubber Consideration Committee and a procedure for the analysis of rubber goods as proposed to be sent to the Council of the American Chemical Society for adoption. Analytical Committee report. Specification Committee report.

STANDARD SAMPLE OF PHOSPHATE ROCK

The Committee on Phosphate Rock, Division of Fertilizer Chemists, American Chemical Society, has received a number of requests from chemists interested in the analysis of phosphate rock for a standard sample of this material. In response to these requests the Committee has decided to adopt as a tentative standard a sample of phosphate rock on which a large number of results have been obtained in coöperative work by members of this Division under the direction of the Committee. The average results obtained in this coöperative work will be furnished with this sample and while these results may not be absolutely correct, yet they are undoubtedly very close to the truth, as they represent an average of the best results obtained, most of them from analysts specializing in this line with the elimination of obviously erratic results. This standard should serve to bring about a greater uniformity in results, both by enabling those interested to check the work of analysts, as well as by enabling the individual analyst to check his own work with a sample of known composition.

Samples may be obtained from Mr. C. F. Hagedorn, Armour Fertilizer Works, Union Stock Yards, Chicago, Illinois, by enclosing 25 cents to cover cost of packing, mailing, etc.

F. B. CARPENTER,
Chairman of Committee on Phosphate Rock

AMERICAN ELECTROCHEMICAL SOCIETY—TWENTY-THIRD GENERAL MEETING

The general meeting of the American Electrochemical Society was held in Atlantic City, New Jersey, April 3rd-5th, with headquarters and meetings at the Hotel Traymore.

PAPERS READ AND DISCUSSED

Presidential Address by *President W. Lash Miller*, introducing the Symposium on the Electrodeposition of Metals.

Electrodeposition of Gold and Silver. *Francis C. Frary*.

Electrodeposition of Copper. *C. W. Bennett*.

Electrodeposition of Brass and Bronze. *C. W. Bennett*.

Electrodeposition of Cobalt and Nickel. *O. P. Watts*.

Electrodeposition of Lead. *F. C. Mathers*.

Solid, thick Lead Cathodes from Lead Acetate Solutions. *F. C. Mathers*.

Solid, thick Lead Cathodes from Lead Lactate Solutions. *F. C. Mathers and B. W. Cockrum*.

Conduction and Radiation of Heat. *I. Langmuir*.

Experiments with Furnace Electrodes. *F. A. J. FitzGerald and A. T. Hinckley*.

Aluminum Nitride. *J. W. Richards*.

Some Tests of the Edison Storage Battery. *C. W. Bennett and H. N. Gilbert*.

Concentration Cells Containing Organic Liquids Immiscible with Waters. *R. Beutner*.

Concentration Changes in Copper Sulfate Electrolysis. *C. W. Bennett and C. O. Brown*.

The 3-Phase 2-Phase Induction Furnace. *A. E. Greene*.

Making Electric Steel without Slag. *A. E. Greene*.

Evening Lecture—Hyperbasis. *Prof. F. B. Kenrick*, of Toronto.

Friday, April 4th, was spent in an excursion to Philadelphia where the making of crucible steel was seen and a two-ton Roebling-Rodenhauser induction steel furnace inspected at the works of the Crucible Steel Casting Co. Visits were also made to the Harrison Bros. Co. (Lead Paints, Lithophone and Contact Sulfuric Acid) and the United Gas Co. Works (Water Gas, Illuminating Gas, and Gas Testing Laboratory).

THE REPORT OF THE SECRETARY OF THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY¹

The preparatory work for this meeting began June 11, 1910. Organization for practical work was fully effected in the United States by June, 1911. The 11 American committees then formed contained upwards of 900 American chemists (not allowing for duplications, which probably did not exceed 10 per cent.). The United States Government and the Governors of 49 States, Ter-

ritories, Insular Possessions of the United States and the Commissioners of the District of Columbia, as well as 30 societies, were further included in these committees by specially appointed representatives, numbering 124 in all.

In March, 1911, the Government of the United States sent formal invitations to all the governments of the world to join in this Congress. Twenty-eight foreign governments accepted and sent a total of 107 delegates. In 18 countries separate organizing committees were formed or organizers were installed, containing upwards of 573 individuals (not allowing for duplications, which probably did not exceed 10 per cent.), and 55 societies and educational institutions.

The Executive Committee of this Congress especially invited 1,483 different technical, scientific and trade societies and educational institutions the world over to join the Congress. Two hundred and thirty-seven in 28 different countries accepted this invitation and appointed 348 delegates.

The total working force in the interests of this Congress the world over amounted therefore to not less than 2,000 individuals (not allowing for duplications, which probably did not exceed 10 per cent.), 392 societies and educational institutions, and 75 governments (including State governments of the United States).

On the publicity side the American Committee placed upon its mailing list 438 trade, technical and scientific publications the world over, and all were supplied with the various publications and appropriate news items from time to time. There were distributed by the Congress, and also on its behalf by American societies, such as the American Chemical Society, the American Electrochemical Society and the Chemists' Club, upwards of 300,000 pieces of printed matter describing the expectations, aims and hopes of this Congress, as well as its accomplishments to date, from about forty different points of view.

Communication was established with central organizing committees in Austria, Hungary, Belgium, Denmark, France, Germany, Great Britain, Greece, Japan, Netherlands, Dutch East Indies, Norway, Russia and Sweden and organizers were installed in Argentina, Chile, Italy and Portugal through whom publicity was maintained, as well as memberships solicited.

The American Sectional Presidents and their Sectional Executive Committees of the 24 different sections themselves by letter solicited papers from specialists the world over. Of these 24 only 17 sections kept a record of such outgoing matters, and these 17 sections sent out 17,176 letters for that purpose.

The net result of the work of this organization the world over is a total of 4,163 members residing in 36 different countries, of which 1,883 coming from 27 different countries, attended the Congress meeting and registered, but more than 9 per cent. failed to bring their membership credentials with them although specifically requested so to do. Of these 1,883 members only 228 or 12 per cent. registered for sections; 1,284 papers were promised or submitted for the Congress; 304 of these were never supplied. Of the papers presented 20 per cent. were rejected either by the Sectional Committee or by the Committee on Papers and Publications, or by both committees. Of the 789 papers accepted by the Congress 560 or 71 per cent. were in print before the Congress assembled in New York. The remaining 229 papers appear in the Appendix. One thousand, three hundred and twenty-two members withdrew their sets of the first 24 volumes of the original communications, and of these not fewer than 514 shipped them directly out of New York City leaving not to exceed 808 sets available for use in preparing discussions; no doubt only a very few of these 808 were used for any such purpose, which was the exact purpose for which so much additional labor and effort were expended.

Two hundred and seventy-seven ladies residing in 12 different countries acquired attendance cards, and of these 246 registered and attended the social functions of the Congress.

The work of the 24 sections was accomplished in 146 meetings

¹ Report, Eighth International Congress of Applied Chemistry, Vol. 28.

TABLE I—SUMMARY OF THE WORK OF THE CONGRESS

	Meetings held	Attendance	Duration Minutes	Papers		Resolutions offered	Papers car- ried over	Left-over papers read later	Papers read by			Exhibits and specimens	Lan- tern	Experiments	Participants in discussions	Minutes used		
				Read	Discussed				Author	Substitute	Title					Reading	Discussing	Extra
Sectional meetings	118	3956	10127	546	252	24	147	81	286	129	131	38	8	3	610	4597	2987	2543 (25%)
Joint meetings.....	28	5747	2873	157	80	1	25	5	96	23	38	17	13	4	250	1603	929	341 (11%)
Grand total.....	146	9703	13000	703(a)	332	25(b)	172(c)	86	382	152	169	55	21	7	860	6200	3916	2884 (22%)

(a) 86 papers, or 11 per cent. of the total, were not in any way presented to the Congress and were therefore of no interest whatever to it.
 (b) 172 papers, or 22 per cent. of the total, were carried over from the assigned program because of the absence of the author or his representative.
 (c) Of these 25 resolutions 9 were laid before the Congress by the Commission of International Congresses of Applied Chemistry; the remaining 16 failed to be brought up for final action because of the failure of their sponsors to attend to the necessary details required by the constitution and by-laws of the Congress.

TABLE II—SUMMARY OF EACH MEETING PERIOD

Sect. Time	Meetings held	Attend- ance	Duration Minutes	Papers		Resolu- tions offered	Papers carried over	Left- over papers read later	Papers read by			Exhibits and spec- imens	Lan- tern	Experi- ments	Partici- pants in discus- sions	Minutes used to	
				Read	Dis- cussed				Sub- stitute	Title						Read	Discuss
6 A.M.	Sectional 21	558	1655	65	31	2	39	..	33	21	18	4	3	..	67	711	342
P.M.	sectional 13	542	1173	60	30	..	44	8	36	10	11	7	1	..	63	507	354
	joint 1	200	150	2	2	2	60	..
	total 14	742	1323	62	30	..	44	8	38	10	11	7	3	..	63	567	354
7 A.M.	sectional 13	430	1209	46	29	1	33	6	22	12	7	4	1	..	79	532	436
	joint 3	385	285	16	14	..	14	..	8	7	1	1	57	131	189
	total 16	815	1494	62	43	1	47	6	30	19	8	5	1	..	136	663	625
P.M.	joint 1	1800	60	1	1	1	60	..
9 A.M.	sectional 17	652	1517	94	53	5	13	11	59	26	9	3	..	1	111	764	537
	joint 2	202	215	15	8	..	1	..	6	2	7	27	82	116
	total 19	854	1732	109	61	5	14	11	65	28	16	3	..	1	138	846	753
P.M.	sectional 10	376	741	41	16	..	5	1	22	11	8	1	44	295	185
	joint 3	313	270	16	8	..	1	1	7	2	7	1	1	1	8	130	45
	total 13	689	1011	57	24	..	6	2	29	13	15	1	2	..	52	425	230
10 A.M.	sectional 13	539	1185	60	29	8	6	9	35	13	12	4	1	..	80	637	373
	joint 3	423	318	18	9	..	5	1	10	3	5	2	23	222	107
	total 16	962	1503	78	38	8	11	10	45	16	17	6	1	..	103	859	480
P.M.	sectional 8	274	659	36	12	6	4	7	17	5	14	6	..	2	38	196	198
	joint 2	319	230	11	9	..	1	..	11	3	4	1	21	120	88
	total 10	593	889	47	21	6	5	7	28	5	14	9	4	3	59	316	286
11 A.M.	sectional 5	88	399	22	14	..	7	3	13	6	3	36	207	99
	joint 2	1030	185	7	4	5	..	2	..	1	..	15	102	80
	total 7	1118	584	29	18	..	7	3	18	6	5	1	51	309	179
P.M.	sectional 3	78	215	16	7	..	7	3	8	..	8	3	2	..	18	103	62
	joint 7	946	640	41	17	1	2	3	25	8	8	7	3	2	52	452	167
	total 10	1024	855	57	24	1	9	6	33	8	16	10	5	2	70	555	229
12 A.M.	sectional 11	366	1116	79	27	28	33	14	32	7	63	530	289
	joint 3	99	290	18	10	..	1	..	15	1	2	1	33	169	110
	total 14	465	1406	97	37	..	1	28	48	15	34	8	96	699	399
P.M.	sectional 4	71	325	13	4	2	..	5	3	2	9	17	85	110
	joint 1	30	130	11	3	5	..	6	1	4	95	27
	total 5	101	455	24	7	2	..	5	8	2	15	1	21	180	137

118 sectional meetings and 28 joint meetings), various details in connection with which are given in Table I.

It appears therefore that the averages of the main features per sectional meeting and per joint meeting were as follows:

	Sectional meeting	Joint meeting
Attendance per meeting.....	34	205
Duration of meeting.....	86 minutes	96 minutes
Papers read per meeting.....	4 1/2	5 1/2
Papers discussed per meeting.....	2	3
Participants in discussion per meeting.....	5	9
Minutes for reading a paper.....	8 1/2	10
Minutes for discussing a paper.....	12	11

About 48 per cent. of the papers presented in Sectional meetings were discussed and about 53 per cent. of the papers presented at joint-meetings; about two-thirds as much time was spent in discussing as in reading papers at sectional meetings and about three-fifths as much in discussing as in reading papers at joint meetings.

THE ATTENDANCES

Taking the final total registration as a basis and assuming further that only members were present (which is manifestly not thoroughly fair basis or assumption, but the best measure that

can be conveniently applied) it appears that the attendance upon these 146 meetings, for each meeting period (of which there were 12 of 2 hours each), ranged from 5.4 per cent. at the last meeting period to 95.6 at the meeting of Saturday afternoon, September 7th, as shown in the following table:

Session of			Attendance	Per cent. of total registration
September 6	forenoon.....	558	29.6	
	afternoon.....	742	39.4	
September 7	forenoon.....	815	43.2	
	afternoon.....	1800	95.6	
September 9	forenoon.....	854	45.4	
	afternoon.....	689	36.6	
September 10	forenoon.....	962	52.1	
	afternoon.....	593	31.5	
September 11	forenoon.....	1118	59.4	
	afternoon.....	1024	54.4	
September 12	forenoon.....	465	24.7	
	afternoon.....	101	5.4	
Grand average attendance 44.5 per cent.				

THE MEETING PERIODS

As provided for in the program there was a total of 12 meeting periods containing a total of 530 meeting hours, or 265 meetings

TABLE III—SUMMARY OF THE SECTIONAL MEETINGS

	Meetings held	Attendance	Duration Minutes	Papers		Resolutions offered	Papers carried over	Left-over papers read later	Papers read by			Exhibits and specimens	Lantern	Experiments	Participants in discussions	Minutes used to		Range of attendance		
				Read	Discussed				Author	Substitute	Title					Read	Discuss	Max.	Min.	Av.
I. Analytical Chemistry.....	6	240	480	29	10	4	9	1	23	1	5	2			21	180	75	50	27	40
II. Inorganic Chemistry.....	5	295	396	28	11	1	1	3	12	9	7	4			24	221	80	145	8	59
IIIa. Metallurgy and Mining....	5	210	385	24	10	4	15	3	11	2	11	5	4		18	194	97	62	10	42
IIIb. Explosives.....	6	284	480	23	6	1	6	7	14	4	5				15	285	95	50	38	42
IIIc. Silicate Industries.....	2	32	150	13	6			5	4	7	2	2			12	10		16	16	16
IV. Organic Chemistry.....	8	531	715	65	33		25	27	38	11	16	7		3	69	468	195	110	25	67
IVa. Coal-Tar Dyes.....	1	29	125	5	3				4	1					9	68	45	29	29	29
Va. Sugar.....	7	147	496	31	10		3	2	17	6	8	3			18	237	87	31	12	21
Vb. India Rubber.....	5	143	182	11	5		3	4	6		5	2			18	79	55	78	11	29
Vc. Fuels and Asphalt.....	3	80	260	10	4		7	1	6		4	1			12	75	115	35	15	27
Vd. Fats, Fatty Oils and Soaps..	2	25	130	5	3		1		4	1					12	72	53	24	1(7)	13
Ve. Paints, Oils and Varnishes..	8	367	657	18	15		5	3	15	3		2	1		71	312	202	69	23	46
VIa. Starch, Cellulose and Paper	8	198	530	29	17	1	2	1	13	2	14	1			48	155	308	36	15	25
VIb. Fermentation.....	6	131	885	35	15	1			11	22	2	1			30	612	205	38	12	22
VII. Agricultural Chemistry....	8	259	770	62	24		20	7	25	20	17	5			62	238	181	46	19	32
VIIa. Hygiene.....	4	104	503	19	14	3	7	6	16	3					29	225	148	44	7	26
VIIb. Pharmaceutical Chemistry	9	265	855	18	13	5	1	3	3	15					25	290	450	50	20	29
VIIc. Bromatology.....	7	152	550	45	5	3	2	5	10	6	29				11	113	50	29	14	22
VIIId. Biochemistry.....	4	96	210	12	(a)				11		1				(a)	(a)	(a)	40	6	24
IX. Photochemistry.....	6	122	705	33	30				20	12	1		3		59	336	304	36	10	20
Xa. Physical Chemistry.....	2	147	113	9	4		6		6	1	2	3			7	94	19	112	35	74
Xb. Electrochemistry.....	3	85	250	13	7		22	3	13						20	201	83	50	20	28
XIa. Law and Legislation.....	3	44	300	9	7	1	12		4	3	2				20	132	140	20	12	15
XIb. Pol. Econ. and Conservation	0																			
Totals.....	118	3956	10127	546	252	24	147	81	286	129	131	38	8	3	610	4597	2987	145	6	34

(a) No record by Sectional Secretary under this heading.

TABLE IV—SUMMARY OF THE JOINT MEETINGS

Sections and Societies	Meeting period	Attendance	Duration Minutes	Papers			Resolutions carried over	Left-over papers read later	Papers read by			Exhibits and specimens	Lantern	Experiments	Participants in discussions	Minutes used to		
				Read	Discussed	Offered			Author	Substitute	Title					Read	Discuss	
4a, 5e, 9.....	6P	200	150	2					2				2				60	
3a, 10a, 11b, A. I. M. E.....	7A	200	95	6	6		2		4	2					23	46	47	
3b, 11a.....	7A	40	70	3	2		12		3						9	65	60	
2 and 3a.....	7A	145	120	7	6				1	5	1	1			25	20	82	
2, 7 10b, 10a.....	7P	1800	60	1					1				1			60		
2, 10a, 10b, A. E. C. S.....	9A	150	120	8	6		1		5	1	2				18	59	51	
5c and 11b.....	9A	52	95	7	2				1	1	5				9	23	65	
8a and 8c.....	9P	58	105	6	2		1		4		2				5	45	25	
4a and 6a.....	9P	55	45	6	2				2	2	2				3	35	20	
2, 3a, 10a, 10b, A. E. C. S.	9P	200	120	4	2			1	1		3	1	1	1		50		
6a, 10a, A. E. C. S.....	10A	250	105	7	3				4		3				8	78	27	
1 and 5c.....	10A	75	110	7	3				2	3	2				9	80	50	
4 and 4a.....	10A	98	103	4	3		5	1	4			2			6	64	30	
10a, 11b.....	10P	250	120	3	3				3			1	1	1	8	55	41	
1 and 5c.....	10P	69	110	8	6		1		8			2	3		13	65	37	
2, 7, 10a, 10b.....	11A	1000	60	1					1			1	1			60		
3a and 5c.....	11A	30	125	7	4				5		2		1		15	42	80	
2, 3a, 10b.....	11P	50	120	6	3				6			3	2	2	5	88	15	
5a, 10a.....	11P	65	120	6	4	1			4	2					20	38	65	
6a and 6b.....	11P	23	70	8	1				3	3	2	2			1	62	3	
5c and 11b.....	11P	40	145	12	3				4	2	6	1	1		7	90	47	
4 and 5b.....	11P	298	50	1	0				1							50		
4 and 5b.....	11P	420	60	5	3	2		3	4	1					10	87	13	
1, 8b, 8c.....	11P	50	75	3	3				3			1			9	37	24	
5c, 11b.....	12A	35	140	9	4				7		2				6	110	30	
5b, 6a.....	12A	14	35	4	1				4						4	6	25	
1 and 3a.....	12A	50	115	5	5		1		4	1		1			23	53	55	
5c, 11b.....	12P	30	130	11	3				5		6	1			4	95	27	
Totals.....	28	5747	2873	157	80	1	25	5	96	23	38	17	13	4	250	1603	929	

in all. The time actually consumed in meetings was 217 hours or 41 per cent. of the time provided and 146 separate meetings were held. This last figure must be augmented by the number of sections participating in joint sessions since each joint session is a meeting for each section, *i. e.*, 39 meetings more than 146 were held or the equivalent of 185 sectional meetings or 80 meetings, *i. e.*, 30 per cent. short of program capacity.

Table A (p. 347) shows the joint and sectional meetings reported by the Sectional Secretaries.

Each section could have met at most 12 times. Table B (p. 347) shows the extent to which this possibility was utilized:

A summary of the work of each meeting period is presented in Table II, showing the details of the sectional and joint meetings of each of the 12 meeting periods.

The detail of the total work of each section in its sectional meetings is given in Table III.

The detail of the total work of each joint meeting is given in Table IV.

TABLE A

Section	Joint meetings	Sectional meetings	Total meetings	Section	Joint meetings	Sectional meetings	Total meetings
1	4	6	10	6a	4	8	12
2	6	5	11	6b	1	6	7
3a	6	5	11	7	2	8	10
3b	1	6	7	8a	1	4	5
3c	0	2	2	8b	1	9	10
4	3	8	11	8c	2	7	9
4a	3	1	4	8d	0	4	4
5a	1	7	8	9	1	6	7
5b	3	5	8	10a	8	2	10
5c	7	3	10	10b	5	3	8
5d	0	2	2	11a	1	3	4
5e	1	8	9	11b	6	0	6
Totals				67	118	185	

TABLE B

Number of meetings	Number of section
12	VIa
11	II; IIIa; IV
10	I; Vc; Ve; VII; VIIIb; Xa
9	VIIIc
8	Va; Vb; Vb
7	IIIb; VIIb; IX
6	XIb
5	VIIIa
4	IVa; VIIId; XIa
2	IIIc; Vd

THE PAPERS

The total number of papers presented to the Congress was 89; of these 560 or 71 per cent. were in print at the opening of the Congress; the remaining 229 were printed in the appendix; 47 papers or 18.63 per cent. of the whole number were illustrated. The following tables contain detail of information:

TABLE V—PAPERS PRINTED BEFORE THE CONGRESS OPENED

Sec.	Papers		Languages used			
	Pages of text	Illustrated	English	French	German	Italian
1	460	48	12	35	13	0
2	246	30	9	17	9	4
3a	150	13	5	12	0	1
3b	150	19	4	15	2	0
3c	131	14	5	14	0	0
4	264	36	3	31	1	4
4a	24	3	0	1	2	0
5a	104	15	1	9	3	3
5b	92	8	3	4	3	1
5c	334	33	12	27	3	3
5d	36	6	1	5	0	1
5e	212	19	5	16	2	1
6a	294	34	12	31	2	1
6b	278	28	4	21	5	2
7	371	53	5	39	12	2
8a	50	5	0	3	2	0
8b	95	14	0	14	0	0
8c	358	39	3	30	7	1
8d	282	39	4	19	16	2
9	280	33	6	33	0	0
10a	209	21	11	20	0	1
10b	252	27	11	21	3	3
11a	79	13	0	2	11	0
11b	193	10	2	10	0	0
Totals	4944	560	118	429	96	31

TABLE VI—PAPERS PRINTED AFTER THE CONGRESS CLOSED

Sec.	Papers		Languages used			
	Pages of text	Illustrated	English	French	German	Italian
1	104	7	2	6	0	1
2	81	10	2	7	1	2
3a	23	6	1	4	2	0
3b	107	7	2	6	1	0
3c	12	2	0	1	1	0
4	136	31	2	21	6	4

TABLE VI—Continued

Sec.	Papers		Languages used			
	Pages of text	Illustrated	English	French	German	Italian
4a	16	4	0	4	0	0
5a	84	15	0	4	11	0
5b	60	5	2	5	0	0
5c	154	28	2	21	1	6
5d	6	1	0	0	0	1
5e	21	3	0	5	0	0
6a	32	6	0	2	0	4
6b	54	11	1	6	0	2
7	80	10	0	9	1	0
8a	152	13	4	15	0	0
8b	34	5	0	4	0	1
8c	60	12	2	10	0	1
8d	8	2	0	0	2	0
9	32	5	1	4	1	0
10a	112	11	5	11	0	0
10b	84	14	2	12	0	2
11a	46	7	0	1	0	6
11b	130	14	1	14	0	0
Totals	1628	229	29	171	27	30

TABLE VII—TOTALS OF DETAILS OF ALL PAPERS PRINTED

Sec.	Papers		Languages used			
	Pages of text	Illustrated	English	French	German	Italian
1	564	55	14	41	13	1
2	327	40	11	24	10	6
3a	173	19	6	16	2	0
3b	257	26	6	21	3	2
3c	143	16	5	15	1	0
4	400	67	5	52	7	8
4a	40	7	0	5	2	0
5a	188	30	1	13	14	3
5b	152	13	5	9	3	1
5c	488	61	14	48	4	9
5d	42	7	1	5	0	2
5e	233	22	5	19	2	1
6a	326	40	12	33	2	5
6b	332	39	5	30	5	4
7	451	63	5	48	13	2
8a	202	18	4	16	2	0
8b	129	19	0	18	0	1
8c	418	51	5	40	7	2
8d	290	41	4	19	18	2
9	312	38	7	37	1	0
10a	321	32	16	31	0	1
10b	336	41	13	33	3	5
11a	125	20	0	5	11	6
11b	323	24	3	24	0	0
Totals	6572	789	147	600	123	61
Per cent.	100	18.63	76.04	15.59	7.73	0.64

DISCUSSIONS

Table I shows that a grand total of 332 papers were discussed by a grand total of 860 participants. However, the discussions printed in volume 27 show that only 172 were discussed and by only 439 participants (*i. e.*, 247 different individuals or 13.1% of the registered attendance) and reported for publication. It appears therefore that the discussion of 160 papers or 48 per cent. and of 421 participants or 49 per cent. failed of finding a place in the final printed volume. The reasons therefor are probably correctly stated in the last paragraph on page 326 of THIS JOURNAL. Table VIII shows the detail of the recorded discussions.

PARTICIPATION IN THE SECTIONS

From Table VII it appears that papers in the English language were offered in each of the 24 sections; that papers in the French language were offered in 20 of the 24 sections, in the German language in 18 of the 24 sections, and in the Italian language in 3 of the 24 sections. It further appears that in the sections

on Fats, Fatty Oils and Soaps, Pharmaceutical Chemistry, Physical Chemistry and on Political Economy and Conservation of Natural Resources, writers in the French language made no original communications; that in the Sections on Metallurgy and Mining, Silicate Industries, Coal-tar Colors and Dyestuffs,

Hygiene, Photochemistry and on Political Economy and Conservation of Natural Resources, writers in the German language made no original communications and that writers in the Italian language made original communications only in Metallurgy and Mining, in Bromatology and in Biochemistry.

REPORTS TO THE CONGRESS

Of the eighteen reports from Committees or Commissions that should have been made to the Eighth Congress only two were received and these were ordered printed, which has been done.

MEMBERSHIP AND REGISTRATION

The total membership in the Congress was 4,163 members from 36 different countries and 277 lady members from 12 different countries, the grand total membership being 4440 from 36 different countries.

The attendance was 1883 members from 27 different countries and 246 ladies from 12 different countries, the grand total attendance being 2129 from 27 countries.

FACTORY INSPECTION AND WORKS VISITS

Members of the Congress in parties of larger or smaller number and all of them in charge of the Committee on Excursions visited and inspected 146 different private chemical manufacturing plants in 24 different cities; this, in addition to a large number of private manufacturing plants of general interest as well as many public, municipal, State and Federal institutions operating along chemical lines; they further visited many public institutions and undertakings in those 24 cities and in 13 other cities, where they were officially received and entertained.

In addition to these official parties many members visited such private chemical plants both before and after the Congress but of these visits no record is here made.

This report cannot be closed without bringing to the notice of the Congress the thorough, complete and most loyal coöperation of the Rumford Press in executing the difficult and trying work of printing the Report of this Congress under exacting and harassing conditions, of Mr. Thomas A. Edison and his entire staff in originating a suitable device for recording discussions and of Miss C. E. Davidson in organizing a corps of transcribers and stenographers to reproduce these recorded discussions in type-writing. The assistance derived from all of these was of the utmost value to the Congress and far beyond any monetary consideration involved. Any shortcomings in the work of these are not due to any faults or omissions of theirs or of their aids, but are due substantially entirely to the failure of members of this Congress to do their share properly and promptly.

Respectfully submitted,

BERNHARD C. HESSE, *Secretary*

NEW YORK, MARCH 31, 1913

FINAL SHIPMENT OF EIGHTH INTERNATIONAL CONGRESS REPORTS, VOLUMES 25-29

The shipment of the last five volumes of the Proceedings of Eighth International Congress of Applied Chemistry began in March and is proceeding as rapidly as possible. This involves the sending of 4395 packages to 3036 different addresses in the United States, the total weight being 80,650 pounds. In addition to this, 37,000 pounds go abroad.

Shipping is being done by express collect. Each member will receive a letter of advice from the Rumford Press together with the express company's receipt. This receipt is to be used by the members and their local express agents to trace delayed or lost shipments.

TABLE VIII—DISTRIBUTION OF PAPERS, DISCUSSIONS OF WHICH WERE PRINTED IN VOLUME 27

Sec.	Vols. 1-24	Appendix	Total	No. of participants reported
1	17	3	20	56
2	8	1	9	21
3a	1	1	2	4
3b	8	1	9	14
3c	1	0	1	2
4	6	6	12	25
4a	1	2	3	7
5a	5	5	10	23
5b	2	1	3	8
5c	10	5	15	45
5d	2	1	3	7
5e	15	2	17	62
6a	8	0	8	13
6b	1	0	1	2
7	21	6	27	70
8a	0	1	1	1
8b	3	0	3	4
8c	7	1	8	16
8d	1	0	1	1
9	0	0	0	0
10a	11	7	18	56
10b	0	0	0	0
11a	1	0	1	2
11b	0	0	0	0
Totals	129	43	172	439

TABLE IX—MEMBERSHIP AND REGISTRATION

Country	Members		Ladies		Grand total	
	Total	Reg.	Total	Reg.	Total	Reg.
Africa.....	9	1	9	1
Argentina.....	81	0	81	0
Australia.....	6	4	1	1	7	5
Austria.....	113	27	8	8	121	35
Belgium.....	16	5	2	2	18	7
Brazil.....	4	2	4	2
Bulgaria.....	1	1	1	1
Canada.....	83	38	6	6	89	44
Chile.....	21	2	1	1	22	3
China.....	2	2	2	2
Cuba.....	6	1	1	1	7	2
Denmark.....	5	5	5	5
Dutch E. Indies.....	1	0	1	0
France.....	185	21	5	4	190	25
Germany.....	219	177	31	22	250	199
Great Britain and Ireland.....	99	46	13	13	112	59
Greece.....	23	0	23	0
Hungary.....	24	8	24	8
India.....	4	0	4	0
Italy.....	43	9	43	9
Japan.....	21	13	21	13
Malay States.....	1	0	1	0
Mexico.....	6	2	6	2
New Zealand.....	2	1	2	1
Netherlands.....	16	7	16	7
Norway.....	26	4	1	1	27	5
Paraguay.....	1	0	1	0
Peru.....	1	0	1	0
Portugal.....	15	3	1	1	16	4
Russia.....	56	27	56	27
Spain.....	23	1	23	1
Sweden.....	6	2	6	2
Switzerland.....	4	1	4	1
Turkey.....	1	1	1	1
West Indies.....	2	0	2	0
United States.....	3037	1472	207	186	3244	1658
Totals	4163	1883	277	246	4440	2129

NOTES AND CORRESPONDENCE

AN APPLICATION OF THE ELECTRIC RESISTANCE FURNACE TO THE DETERMINATION OF OXYGEN IN IRON AND STEEL. A CRITICISM

Editor of the Journal of Industrial and Engineering Chemistry:

IN THIS JOURNAL, 5, 123, appears an article on the application of the electric resistance furnace to the determination of oxygen in iron and steel.

The writer's¹ modification of the Ledebur method is referred to, and the double electric furnace as well as certain other modifications are proposed as improvements.

The laboratories under the writer's supervision have had probably a larger and wider experience with the determination of oxygen in iron and steel than any other in this country. In our opinion the modifications proposed by McMillen present no improvements over the process used by us, and are open to criticism in respect to several important points. In a routine laboratory where a large number of oxygen determinations have to be made, the time element is of great importance. With the gas blast furnace, using a silica tube it is possible to cool down immediately by turning on the cold air blast, so that accurate results can be obtained in one-half hour. The double electric furnace modification runs the test for a full hour, and if the analysis is started with a cold furnace, it will require an hour to reach the specified temperature of 950° C., whereas the gas blast furnace can be brought to temperature in a few minutes. In our practice we often exceed this temperature and have never found that we obtain higher results with the higher temperatures.

McMillen proposes the use of a porcelain boat instead of the nickel boat used by us. We especially avoided the use of porcelain, owing to the tendency of that material to adsorb moisture from the air.

The most important criticism of McMillen's modification that we have to offer is with respect to weighing the phosphoric acid absorption tube filled with hydrogen. We believe this to be bad practice, and numerous tests made in this manner have shown discordant results owing to the tendency of hydrogen to diffuse through "air tight" stoppers.

The McMillen method is almost identical with the one published by the writer, with the exception of the points discussed above, and for the reasons stated it does not appear that any contribution has been made to the older method. McMillen again points out the well-known fact that the Ledebur method will not determine total oxygen, owing to the fact that certain oxides and silicates are not reducible by hydrogen. Walker and Patrick² have proposed a method for determination of total oxygen, by making use of a vacuum electric furnace of the Arsem type. The installation for this method is very expensive and at best it could hardly become a routine determination in any chemical laboratory. On the other hand, it should not be forgotten that in most cases it is only the determination of oxygen combined with iron that yields the data desired, and it is this information which can be readily obtained by the Ledebur method. The amount of oxygen combined with silica and other oxides unreducible by hydrogen has no bearing on the question as to whether iron or steel is properly deoxidized in the process of manufacture.

ALLERTON S. CUSHMAN

INSTITUTE OF INDUSTRIAL RESEARCH
WASHINGTON, FEB. 26, 1913

¹ THIS JOURNAL, 3, 372.

² *Ibid.*, 4, 799.

AN ACCURATE VISCOSIMETER WITH PRACTICAL QUALITIES

Editor of the Journal of Industrial and Engineering Chemistry:

The statement of W. F. Faragher concerning "A Standard Viscosimeter" in THIS JOURNAL, 5, 167, is, unfortunately, too true to arouse the least hint of denial. Yet we can hardly expect to obtain consistent results with viscosimeters many of which, stripped of all external equipage, are fundamentally dependent on little more than a hole in a can. This statement, which perhaps may seem altogether facetious, will be verified by a glance at the Engler, Redwood and Saybolt types and others in common use.

Where then can we get an instrument of less faulty construction for our standard? Is it necessary to turn to Germany? Let us first look over what our own chemists have to offer. In 1894 the English chemists Thorpe and Rodger published a paper¹ describing a viscosimeter which introduced the foundation principle involved in a very neat and accurate instrument developed later by Bingham and White.² As used by them, however, it was scarcely an implement for practical industrial work until further simplified by White. In an article on the viscosities of blood and blood serum, which appeared in the *Biochemische Zeitschrift*, 37, 482 (1911), the latter gives a detailed description of his viscosimeter, the main points of which are noted below. The instrument consists of two vertical limbs of glass tubing fused into the ends of a horizontal capillary tube of about 0.1 millimeter inside diameter and of length depending upon the viscosity of the substance used; *i. e.*, varying from about 10 centimeters for liquids of small viscosity like water to 2-3 centimeters for the more viscous oils. The limbs are marked so that, by falling from the higher to the lower mark, 3 or 4 cc. of a liquid have passed through the capillary. The volume of the tube between these marks is carefully determined before fusing in the limbs. One limb is also furnished with a trap by means of which the volume used can be regulated. The fluid is forced through the capillary under a known pressure and the viscosity calculated by means of the Poiseuille formula corrected for kinetic energy as shown:

$$\eta = \frac{\pi r^4 p t}{8 v l} - \frac{\rho d}{8 \pi l}$$

The volume (v) having been determined as indicated above, the constants $\frac{\pi r^4}{8 l}$ and $\frac{\rho}{8 \pi l}$ are easily obtained by calibrating with a liquid of known viscosity, such as water. The pressure is measured with a manometer and the temperature regulated by immersing the instrument in a bath.

With regard to the accuracy of the instrument, a few data will serve better than words of praise. The following is taken from work done on fish and vegetable oils at Wood's Hole by White and Thomas:³

VISCOSITY OF DOGFISH OILS			
Temperature Degrees	Right limb	Left limb	Average
30	0.4143	0.4140	0.4142
50	0.2113	0.2110	0.2112
70	0.1247	0.1247	0.1247
90	0.08046	0.08063	0.08055

In order to show that accuracy is attainable not by the inventor only, there are noted below a few results obtained by the writer working on butter fat with an instrument of this style.

Having demonstrated the consistency of results obtained, it remains to be seen whether there are enough points in favor of

¹ *Phil. Trans.*, 185, 397 (1894).

² *Z. physik. Chem.*, 80, 670 (1912).

³ THIS JOURNAL, 4, 378 (1912).

VISCOSITY OF BUTTER FAT

Temperature Degrees	Right limb	Left limb	Average
40	0.3200	0.3203	0.3202
60	0.1644	0.1644	0.1644
80	0.09682	0.09681	0.09682
90	0.07749	0.07759	0.07754

this type to warrant its being considered for adoption as a standard. What are its good features? In the first place it is easily made, the mediocre skill of the ordinary chemist in glass-blowing and a few hours practice being all that is required. It is convenient to handle; nor is it so fragile as to require great care in manipulating. As mentioned above, it is readily calibrated without depending upon the difficult method of actual measurement of bore and length of the capillary. The temperature is easily regulated. The apparatus required can be set up in any laboratory with the materials at hand. Only a few minutes are required for a run and as many runs as desired may be taken by simply changing the pressure from one limb to the other, taking the time as the liquid flows each way. It is by no means of little importance that only 7 to 10 cc. of a fluid are required for any number of determinations necessary. The measurements made with different instruments exhibit none of the discrepancies which, as was pointed out in the article in the January issue, are obtained with instruments in common use. The inaccuracies of the Ostwald viscosimeter and the impracticability of its use with very viscous oils, both serious faults, are not met with. Finally the viscosities obtained are in absolute units and, of course, are comparable with the results obtained by other instruments depending on the same principles.

In conclusion then, is not this instrument, possessing all these good qualities and also adaptability to practical industrial work, worthy of careful consideration before we adopt as a standard a German implement which may prove less advantageous?

R. H. TWINING

CLARK COLLEGE
WORCESTER, MASS., FEB. 24, 1913

COURT DECISION ON THE MANUFACTURE OF CARBORUNDUM

The Circuit Court of Appeals at Philadelphia has just decided in the case of the Electric Smelting & Aluminium Company *vs.* the Carborundum Company of Niagara Falls, that the Alfred H. Cowles patent No. 319,790 is substantially a basic patent for the manufacture of carborundum. This decision is said to involve the payment of more than \$250,000 by the Carborundum Company to the first-named company, which also recovered a large amount some years ago from the Pittsburgh Reduction Company for infringement of a series of electrochemical patents controlled by Mr. Cowles' interests.

NEW GEOLOGICAL SURVEY BUILDING PROVIDED

After a 26-year campaign the United States Geological Survey has received generous recognition at the hands of Congress in the authorization of an expenditure of \$2,596,000 for the construction of a fireproof building of "modern office-building type of architecture." With this sum it is proposed to erect a building on ground already owned by the Government which shall accommodate, besides the Geological Survey, the Reclamation Service, the Indian Office, and the Bureau of Mines, all bureaus of the Interior Department whose work is closely related to that of the Survey and among all of which there is more or less constant cooperation.

The public buildings law, which carries the Survey item, authorizes an immediate appropriation of \$596,000, the balance to be appropriated as needed in construction. While this omnibus building law is only an "authorization" measure, leaving the actual appropriation of the money to a future act, \$96,000 of the amount included in the measure can be expended immediately, having been appropriated by a former Congress in connection with the purchase of the site on which the Survey building is to be erected. Plans can thus go forward at once for the construction of the new building. For the needs of the Survey and the other bureaus mentioned an up-to-date, conveniently arranged, and well-lighted building is of especial importance. Too many of Uncle Sam's great army of civil employees at Washington work in part or exclusively by artificial light, in quarters that may be compared to dungeons, a condition which is suggestive of medieval times, when the first requirement of castles was walls thick enough to resist the attacks of battering rams and catapults, or of the still more ancient period when huge, ornate pillars and columns were the fashion, regardless of the arrangements with respect to light and convenience on the inside of the building. The innovation of providing a structure of the modern office type for government "workshops" in which a maximum of high-grade output is the first consideration, such as will occupy the new building, will be welcomed.

POTASH LANDS WITHDRAWN

The President has recently approved the withdrawal of three tracts of land of the desert-basin type in California and Nevada that are believed, as the result of investigations by the United States Geological Survey, to contain valuable deposits of potassium salts and brines. The survey adds:

The constructive good faith of the Government in the withdrawal of these lands in aid of legislation is indicated by the fact that concurrently with the withdrawal the Interior Department has prepared the draft of a law intended to relieve the present chaotic situation and provide a safe and sure legal basis for the development of the deposits now known and any that may be discovered in the future. This draft has been submitted to Congress for its consideration, and its enactment will be urged in order that American potash deposits may be developed under conditions that are favorable to the producer and will at the same time protect the consumer.

THE RARE EARTH MINERALS

A recent Geological Survey bulletin gives information concerning a valuable Texas deposit of these minerals. Economic interest in them centers in their incandescence on being heated, and owing to this property they have been much sought. Thoria, beryllia, yttria, and zirconia show it in the greatest degree, but thoria and beryllia, which form the bulk of the incandescent oxides used in gas mantles, are too easily volatilized to be used in an electric glower, such as that of the Nernst lamp. Yttria and zirconia, however, will stand the necessary high temperature. Before the discovery of this deposit it was practically impossible to get sufficient yttria-bearing minerals to manufacture the lamps. The needs of the Nernst Lamp Co., which owns the deposit, require only the occasional working of the mine, and after enough yttria is obtained to supply its wants for a few months ahead, the mine is closed. But a few hundred pounds a year are extracted.

BOOK REVIEWS

Chloride of Lime in Sanitation. By ALBERT H. HOOKER. Published by John Wiley & Sons. pp. 231. Price, \$3.00. The relation of sanitation to public health especially under

the ever-increasing congestion of city life is of such importance that the appearance of this book is fully warranted.

The author, Mr. Albert H. Hooker, of the Hooker Electro-

chemical Company, has brought together the data collected by the Research Laboratory of the Company on the use of Chloride of Lime in Sanitation. The subject matter is extremely well arranged, the first part of the work being divided into chapters dealing with the purification of water, sewage treatment, street sprinkling and all the various problems of sanitation. The greater part of the book is devoted to over four hundred abstracts and references from the different engineering, municipal and sanitary journals dealing with the various sanitary problems.

Mr. Hooker is to be congratulated on having produced a volume of so much real value; while the book will be of greatest use to those in charge of work connected with the public health, it will be read with interest and profit by all.

OTTO KRESS

Water, Its Purification and Use in the Industries. By WILLIAM WALLACE CHRISTIE, Consulting Engineer. Published by D. Van Nostrand Company, New York, 1912. 8vo, x + pp. 219, 171 Illustrations, 3 Colored Plates. Price, \$2.00.

The author is already well known to steam power engineers through his books on "Chimney Formulae and Tables," "Chimney Design and Theory," "Boiler Waters" and "Furnace Draft." In this later work he has produced a valuable reference book on water purification for the industries.

The descriptions and illustrations relating to the various water softening processes are especially clear and complete and the colored plates which relate to this subject serve greatly to assist in an understanding of the devices used in industrial water treatment.

The first chapter gives a description of the sources of water and the special properties required in numerous industries, such as concrete construction, brewing, dyeing and bleaching, ice-making, laundry work, soap and paper manufacture, steaming and sugar refining. Then follow three chapters on the various cold and hot processes of water softening and the results accomplished by such treatment.

Chapter V is devoted to a short description of pressure filters and Chapter VI to sterilization, distillation and aeration. Then follows a brief description of slow sand and open mechanical filters. The three final chapters are on the measurement of water, the effect of oil in boiler water and useful information relating to water measurement and treatment.

If the title of the book were "The Purification of Water for Use in the Industries" it would more nearly represent the character of its contents as an adequate consideration of municipal water purification is hardly the intention of the author.

Mr. Christie has given us a most valuable reference work on the treatment of water supply for industrial use and one which will meet the needs of those who desire to get the best results from water used for steaming or other manufacturing purposes.

D. D. JACKSON

The Chemical Analysis of Lead and its Compounds. By JOHN A. SCHAEFFER, A.M., Ph.D., Chief of Laboratory and Director of Research, and BERNARD S. WHITE, Assistant Chemist. Octavo, pp. 63. No illustrations. Published by the Picher Lead Co., Joplin, Mo., for gratuitous distribution.

This little book describes methods for the analysis of lead ores, valuable merchantable furnace products, oxides of lead, basic carbonate of lead, pig lead, etc. The reading of this book indicates that it is designed more for the use of untrained chemists. The preface refers to the demand for "extreme accuracy coupled with rapidity of manipulation." It is doubtful whether the methods described in most cases comply with these requirements.

In the calculations much detail is given, but unfortunately without much regard for algebra or form of expression. Thus, on page 27 we find these two calculations

$$112 : 685 :: 0.005 : X$$

$$X \text{ equals } 3.058$$

$$112 : 239 :: 0.005 : X$$

$$X \text{ equals } 1.067$$

Evidently there is a factor omitted.

Then on page 11 it is stated:

$$0.0025 \text{ equals } \frac{1}{4} \text{ of } 0.01\%$$

where similarly a factor is omitted.

These calculations, if necessary, surely should be complete in the presentation of all the factors.

The details for analysis are hardly as full as they should be to conform with the apparent purpose of the book. Thus, on page 10, in a volumetric determination of lead in lead chromate, the direction is given: "Dissolve the lead chromate in dilute hydrochloric acid (1 : 1), using as little of the acid as possible." Of course, the acid should be cold but this is not specified.

On page 10 where chromic acid is determined volumetrically by a ferrous ammonium sulfate solution, using a two per cent. solution of potassium ferrocyanide as an outside indicator, it would appear that this should preferably read: "potassium ferriocyanide."

Some matters under dispute are stated as proven facts. Thus, on page 18, that sulfate dioxide found in basic lead sulfate "does not exist as a sulfite, but is instead an apparently occluded gas." It seems hardly probable that sulfur dioxide would exist in basic lead sulfate to the extent of a few hundredths of a per cent. as an occluded gas in the presence of over 15 per cent. of lead oxide and 5 per cent. of zinc oxide.

Also on page 19, referring to the determination of apparent density, the authors state that this density is dependent on two factors, the fineness and the density of the particles. On the question of apparent density, from rational consideration it would appear that fineness is less a factor than the condition of sub-division; that is, as the particles approach a uniform size, the apparent density decreases.

On page 43 the authors give typical analyses of basic carbonate of lead for impurities. We would question these analyses being typical as the acetic acid present is excessively high and out of all proportion to what exists in commercial white leads.

In the analysis of pig lead it is to be regretted that the author did not follow Fresenius' general method. Certain modifications of questionable advisability have been introduced. Thus, by Fresenius' method, after the pig lead is dissolved, if a clear solution is obtained or after filtering if a clear solution is not obtained, sulfuric acid is added in a graduated flask and an aliquot portion is taken and evaporated to fumes. The authors add the sulfuric acid and evaporate the whole mass to fumes. This is, to say the least, a hazardous operation, working on 200 grams of lead. Furthermore, following Fresenius' method, nothing is thrown out by the sulfuric acid but lead. It is probable that antimony and perhaps other constituents would be thrown out by following the authors' method of evaporation to fumes before removing the sulfate of lead.

This little book contains much valuable information which, undoubtedly on the printing of a new edition, can be put in somewhat better and more accurate form, as it fills a proper place in the literature of chemical analysis. We would suggest that in such future editions some more up-to-date and well-known methods of analysis be introduced, such as the determination of the true red lead or lead dioxide, as the case may be, in commercial red leads, following Walker's method which gives very accurate and satisfactory results.

G. W. THOMPSON

NEW PUBLICATIONS

By D. D. BERGOLZHEIMER, Librarian, Chemists' Club, New York

- Cerium Metals and Pyrophoric Alloys.** By HEINRICH KELLERMANN. 8vo., pp. 116. Price, \$1.25. Wilhelm Knapp, Halle. (German.)
- Chemical Theory and Calculations.** By F. J. WILSON AND I. M. HEDRICK. Sm. 8vo., pp. 138. Price, \$1.00. D. Van Nostrand Co., New York.
- Cyaniding of Silver Ores. The Chemical Actions during the.** By E. KUEHN. 8vo. Price, \$1.50. Wilhelm Knapp, Halle. (German.)
- Directory of Chemical Industry, 1913, Universal.** ANONYMOUS. 8vo., pp. 1053. Union Deutsche Verlagsgesellschaft, Stuttgart.
- Directory of Chemical Manufacturers, etc., in Great Britain.** Chemical Trade. ANONYMOUS. 5th Ed. 8vo. Davis Bros., London.
- Fats, Lipoids and Waxes, Chemistry of the.** By W. GLIKIN. Vol. II. 8vo. Price, \$18.00. Gebrueder Borntraeger, Leipzig. (German.)
- Flour Manufacture, Processes of.** By PERCY A. AMOS. Cr. 8vo., pp. 280. Price, \$1.50. Longmans, Green & Co., New York.
- General Chemistry, A Course in.** By WILLIAM MCPHERSON AND WILLIAM E. HENDERSON. 8vo., pp. 556. Price, \$2.25. Ginn & Co., New York.
- Iron Foundries and Allied Industries, Chemical Methods of Examination for.** By ALBERT VITA AND CARL MASSENEZ. 8vo. Price, \$1.00. Julius Springer, Berlin. (German.)
- Iron Foundry Chemist, Practice of the.** By CARL KRUG. 8vo. Price, \$1.50. Julius Springer, Berlin. (German.)
- Japanning, A Handbook on.** By W. N. BROWN. 2nd Ed. Cr. 8vo., pp. 70. Price, \$1.00. Scott, Greenwood & Co., London.
- Measurements and Graphical Methods, Precision of.** By H. M. GOODWIN. 8vo., pp. 104. Price, \$1.25. McGraw, Hill Book Co., New York.
- Mechanical Appliances of the Chemical and Metallurgical Industries.** By OSKAR NAGEL. 2nd Ed. 8vo., pp. 300. Price, \$2.25. Vacher & Sons, London.
- Metals, the Rarer, Mineralogy of.** By CAHEN AND WOOTON. 8vo. Price, \$1.50. Chas. Griffin & Co., London.
- Metal Statistics, 1912.** ANONYMOUS. 8vo., pp. 255. American Market and Daily Iron and Steel Report, New York.
- Organic Chemistry II.** By V. V. RICHTER, R. ANSCHUTZ AND H. MEERWEIN. Vol. II, 11th Ed. Price, \$7.00. Friedrich Cohen, Bonn. (German.)
- Organic Compounds.** By J. W. SHEPHERD. 8vo., pp. 348. Price, \$1.75. W. B. Clive, London.
- Organic Compounds, Chemical Technology of.** By R. O. HERZOG. 8vo., pp. 732. Price, \$5.50. Robert Kiepert, Berlin. (German.)
- Organometallic Compounds of Zinc and Magnesium.** By HENRY WREN. 8vo., pp. 100. Price, \$0.50. Gurney & Jackson, London.
- Oil Industries, Chemistry of the.** By J. E. SOUTHCOMBE. 8vo., pp. 204. Price, \$2.00. Constable & Co., London.
- Paper Pulp, Dyeing of.** By JULIUS ERFURT. 3rd Ed. 8vo. Price, \$4.00. Carl Hofmann, Berlin. (German.)
- Patents, Engineers' Handbook of.** By WILLIAM MACOMBER. 8vo., pp. 288. Price, \$2.50. Little, Brown & Co., Boston.
- Qualitative Analysis.** (Translation.) By F. P. TREADWELL AND WM. T. HALL. 3rd Ed. from 5th German Ed. L. 8vo., pp. 534. Price, \$3.00. John Wiley & Sons, New York.
- Sewage Disposal in the United Kingdom, A Textbook on.** By H. L. CANNON. 8vo. Price, \$2.00. St. Bride's Press, London.
- Steels, The Special.** By G. MARS. 8vo., pp. 517. Price, \$4.75. Ferdinand Enke, Stuttgart. (German.)
- Sugar; Investigations on Methods of Analysis of Cane Products.** By WILLIAM E. CROSS. 8vo., pp. 83. Louisiana Agricultural Experiment Station Bulletin 135
- Wood Preservation: Some Facts about Treating Railroad Ties.** By W. F. GOLTRA. Vol. II. 8vo. Price, \$1.00. W. F. Goltra, Cleveland.
- Woolen and Half-Woolen Goods, The Finishing of.** By N. REISER. 2nd Ed. L. 8vo., pp. 695. Price, \$6.75. A. Felix, Leipzig. (German.)
- Coal and Its Wastes.** By W. BOYD CAMPBELL. *Pulp and Paper Magazine of Canada*, Vol. 11, 1913, No. 4, pp. 131-132.
- Coke Ovens, Progress in By-Product Recovery at.** By J. E. CHESTER. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 4, pp. 115-125.
- Dyestuffs and Pigments, Rapid Test for Fastness to Light of.** By KURT GEBHARD. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 11, pp. 79-80.
- Food; Scientific Advancement of the Canning Industry.** By R. T. MOHAN. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 4, pp. 167-171.
- Gas, Water, Purification Material, Analysis of.** By E. C. UHER. *American Gas Light Journal*, Vol. 98, 1913, No. 10, pp. 156-159.
- Hydrochloric Acid Condensation, Rational.** By THEODOR MEYER. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 15, pp. 97-100.
- Ink, New Principles for Official Testing of.** By F. WILLY HINRICHSSEN. *Chemiker Zeitung*, Vol. 37, 1913, No. 27, pp. 265-267.
- Inorganic Chemistry and Electrochemistry in 1912, Experimental.** By A. GUTHRIE. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 17, pp. 105-132.
- Lubrication; Formation of Deposits of Oils in the Cylinders and Bearings of Steam and Power Machines.** By H. SCHLUTER. *Chemiker Zeitung*, Vol. 37, 1913, No. 22, pp. 221-223.
- Nitric Acid in the Presence of Nitrous Acid, New Method of Detecting.** By W. N. IVANOW. *Chemiker Zeitung*, Vol. 37, 1913, No. 16, pp. 157.
- Oxygen in Organic Compounds, The Direct Determination of.** By MAITLAND C. BOSWELL. *Journal of the American Chemical Society*, Vol. 35, 1913, No. 3, pp. 284-290.
- Paper Industry, Contributions to the Technology of the.** By CLAYTON BEADLE AND HENRY P. STEVENS. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 4, pp. 174-179.
- Paper Making, Notes on the Chemistry of.** By THOMAS J. KEENAN. *Paper*, Vol. 10, 1913, No. 11, pp. 27-30.
- Paper, New Sources of Supply for the Manufacture of.** CLAYTON BEADLE AND HENRY P. STEVENS. *Journal of the Royal Society of Arts*, Vol. 51, 1913, No. 7.
- Paper Straw and Strawboard, The Manufacture of.** By LEO SCHLICK. *Pulp and Paper Magazine of Canada*, Vol. 11, 1913, No. 4, pp. 123-125.
- Papers, Testing of Parchmentized.** By V. FORTINI AND H. CECCHERELLI. *Chemiker Zeitung*, Vol. 37, 1913, No. 24, pp. 237-239.
- Retorts, some Notes on Charging and Discharging Machines for.** W. L. HEALD. *American Gas Light Journal*, Vol. 98, 1913, No. 8, pp. 130-134.
- Sewage, The Slate-Bed Treatment of.** By W. J. DIBDIN. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 2, pp. 55-61.
- Starches, Commercial, for Cotton Mill Purposes, The Value of.** By G. M. MACNIDER. *Cotton*, Vol. 77, 1913, No. 4, pp. 158-161.
- Steam Accumulators and Regenerative Processes, Theory of.** By F. G. GASCHE. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 28, 1912, No. 9, pp. 723-794.
- Steam, Exhaust, in the Brewery, Utilization of.** By WM. CLASMAN. *Journal of the American Society of Brewing Technology*, Vol. 3, 1913, Nos. 3 and 4, pp. 83-107.
- Steel Making, Titanium as Used in.** By E. F. LAKE. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 3, pp. 144-146.
- Soil Analysis.** By W. HARRISON MARTINDALE. *Chemist and Druggist*, Vol. 82, 1913, No. 1726, pp. 67-69.
- Sugar Cane; Recent Work on Dry Substance Determination.** By WM. E. CROSS. *Louisiana Planter and Sugar Manufacturer*, Vol. 50, 1913, No. 10, pp. 158-159.
- Sugar in Molasses, A Modification of the Clerget Method of Determining.** By WM. E. CROSS AND W. G. TAGGART. *Louisiana Planter and Sugar Manufacturer*, Vol. 50, 1913, No. 9, pp. 142-144.
- Sugar, Manufacture of Raw, in the Philippine and Hawaiian Islands** By C. A. BROWNE. *School of Mines Quarterly*, Vol. 34, 1913, No. 2, pp. 119-136.
- Sulfur Trioxide in Sulfur Furnace Gases, Determination of.** By ERICH RICHTER. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 17, pp. 132-134.
- Water; The Determination of Moisture.** By G. N. HUNTLEY AND J. H. COSTE. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 2, pp. 62-66.
- Water; The Determination of Moisture in Organic Substances.** By F. H. CAMPBELL. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 2, pp. 67-70.

RECENT JOURNAL ARTICLES

- Blower Sets, The Use of Turbo, in Water Gas Plants.** ANONYMOUS. *American Gas Light Journal*, Vol. 98, 1913, No. 8, pp. 122-126.
- Caoutchouc and Gutta Percha Resins.** By G. H. HILLEN. *Archiv der Pharmazie*, Vol. 251, 1913, No. 2, pp. 94-121.
- Cast Iron, Notes on.** By ALBERT SAUVEUR. *Iron Age*, Vol. 91, 1913, No. 10, pp. 595-598.
- Cement, Portland, The Constitution of.** By P. H. BATES. *Cement and Engineering News*, Vol. 25, 1913, No. 2, pp. 46-48.
- Coal, How to Sample.** By E. G. BAILEY. *Cotton*, Vol. 77, 1913, No. 4, pp. 140-141.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

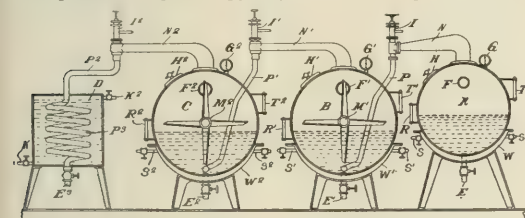
Solidified Hydrogen Peroxid and Process of Forming the Same. F. E. Stockelbach, Feb. 4, 1913. U. S. Pat. 1,051,926. A solid compound of hydrogen peroxide is obtained by dissolving in a solution of the peroxide, a small quantity of acetanilid and a large quantity of urea and then evaporating the solution.

Method of Determining the Content of Butter-Fat in Butter. R. H. Shaw, Feb. 4, 1913. U. S. Pat. 1,052,098. Hot water is added to the butter under examination and the mixture centrifuged. The aqueous solution is drawn off and while the residue is still hot a mixture of equal parts of sulfuric acid and water is added and the mixture centrifuged. The acid solution is drawn off and the residue again centrifuged and weighed.

Process of Refining Sugar. Hermann Wiese, U. S. Pat. 1,052,113. Lime is added to a hot watersolution (above 70° C.) of raw sugar and the resulting mass carbonated until substantially neutral. The sugar solution is then reheated to above 70° C. in the presence of carbonate of lime and filtered.

Manufacture of Acetate of Lime and Wood Alcohol. C. W. Volney, Feb. 4, 1913. U. S. Pat. 1,052,446. By this method it is possible to produce in one operation, a comparatively pure acetate of lime and a comparatively pure wood alcohol.

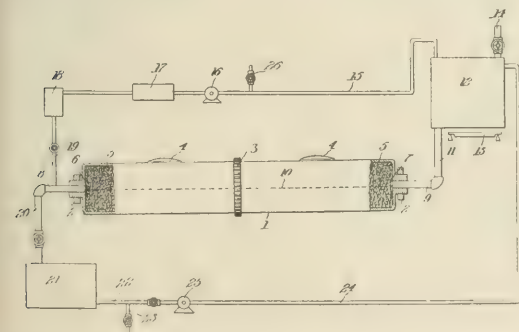
In practice, vapor of pyroigneous acid is passed through



calcium carbonate held in suspension in boiling water.

The vapors arising from the water are then passed through water holding calcium hydrate in suspension and condensed.

Process of Making Edible Oils. Carleton Ellis, Feb. 11, 1913. U. S. Pat. 1,052,469. Materials containing unsaturated bodies are subjected to the action of hydrogen in the presence of a porous mass of catalytic material, a traveling stream of such

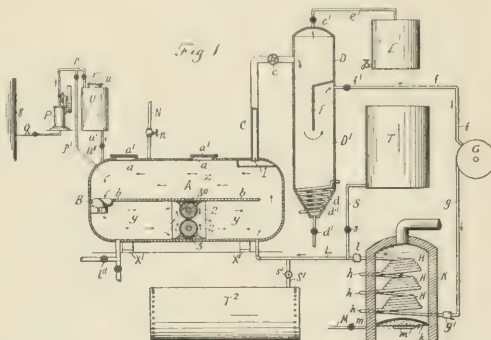


material being passed through a porous mass of catalytic material, moving substantially transversely to the direction of such stream, and simultaneously contacted with such material.

In the accompanying illustration showing apparatus in which the process is practiced, a portion of the barrel containing

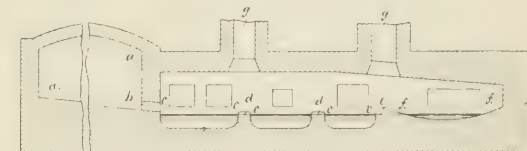
catalytic material is cut away to show the location of the catalyzer.

Process of Making Cellulose. Burdett Loomis, Feb. 11, 1913. U. S. Pat. 1,052,675. In this process, the woody or vegetable fibrous material in a closed chamber is subjected to the action of hot water circulated in contact with it and the softened ma-



terial subjected to the action of a beating drum in the same chamber. The circulating water which contains the gummy and resinous material is drawn off from time to time and the latter separated and collected, the circulation of water and the beating and grinding operation being continued until the material is reduced to cellulose.

Manufacture of Salt. John H. Webster, Feb. 11, 1913. U. S. Pat. 1,052,703. By this process granulated salt is produced directly from fused or melted salt without first having to allow it to solidify into blocks, and subsequently break and crush these blocks into grains of the size required.



In practice, the salt is melted, and while in its molten state it is agitated, or broken up, by mechanical means, while in a body, and it is cooled and solidified while being agitated. The grains of salt thus produced, in most cases, vary in size; and the different sizes of grains or crystals are separated according to requirements by screening.

Process of Treating Ores Preparatory to Magnetic Separation. J. B. Etherington, Feb. 18, 1913. U. S. Pat. 1,053,486. In this process ore containing non-magnetic iron sulfids is subjected to heat in a non-oxidizing atmosphere until the iron sulfids become magnetic and the mass is removed from the action of the heat before the iron sulfids are converted into oxids.

Process for the Reduction of Stannic Oxid. Zdenko Metzl, Feb. 18, 1913. U. S. Pat. 1,053,624. Tin oxid is reduced to metallic tin by reacting upon the oxid with metallic zinc at a temperature at least as high as the melting point of metallic zinc, then volatilizing the zinc oxid and finally subjecting it to the action of a reducing agent to reduce it to metallic zinc.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF MARCH, 1913

ORGANIC CHEMICALS

Acetanilid.....Lb.	21	@	23
Acetic Acid (28 per cent.).....C.	2.00	@	2.15
Acetone (drums).....Lb.	16 1/2	@	17 1/2
Alcohol, denatured (180 proof).....Gal.	37	@	39
Alcohol, grain (188 proof).....Gal.	2.50	@	2.55
Alcohol, wood (95 per cent.).....Gal.	49	@	52
Amyl Acetate.....Gal.	2.35	@	2.55
Aniline Oil.....Lb.	10 1/4	@	10 3/8
Benzoic Acid.....Lb.	23	@	27
Camphor (refined in bulk).....Lb.	42 1/2	@	44
Carbolic Acid (drums).....Lb.	13	@	15
Carbon Bisulfide.....Lb.	6 1/2	@	8
Carbon Tetrachloride (drums).....Lb.	8	@	8 1/2
Chloroform.....Lb.	25	@	35
Citric Acid (domestic), crystals.....Lb.	40	@	40 1/2
Dextrine (corn).....C.	2.60	@	2.81
Dextrine (imported potato).....Lb.	6	@	7
Ether (U. S. P., 1900).....Lb.	14	@	20
Formaldehyde.....Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....Lb.	19 3/4	@	20
Oxalic Acid.....Lb.	8 1/4	@	8 1/2
Pyrogallie Acid (bulk).....Lb.	1.20	@	1.40
Salicylic Acid.....Lb.	29	@	31
Starch (corn).....C.	1.82	@	2.27
Starch (potato).....Lb.	5 1/4	@	5 3/4
Tannic Acid (commercial).....Lb.	35	@	35 1/2
Tartaric Acid, crystals.....Lb.	30 1/4	@	31

INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....Lb.	7 3/4	@	8
Acetate of Lime (gray).....C.	2.50	@	2.60
Alum (lump).....C.	1.75	@	2.00
Aluminum Sulfate.....C.	90	@	1.75
Ammonium Carbonate, domestic.....Lb.	8	@	8 1/2
Ammonium Chloride, gray.....Lb.	6 1/4	@	6 1/2
Aqua Ammonia (drums) 16°.....Lb.	2 1/4	@	2 1/2
Arsenic, white.....Lb.	4 3/8	@	5
Barium Chloride.....C.	1.70	@	1.80
Barium Nitrate.....Lb.	5	@	5 1/4
Barytes (prime white, foreign).....Ton	18.50	@	22.50
Bleaching Powder (35 per cent.).....C.	1.35	@	1 1/2
Blue Vitriol.....Lb.	5 1/4	@	5 1/2
Borax, crystals (bags).....Lb.	3 3/4	@	4 1/4
Boric Acid, crystals (powd.).....Lb.	7	@	7 1/2
Brimstone (crude, domestic).....Ton	22.00	@	22.50
Bromine, bulk.....Lb.	30	@	35
Calcium Chloride.....C.	65	@	90
Chalk (light precipitated).....Lb.	4	@	5
China Clay (imported).....Ton	11.50	@	18.00
Feldspar.....Ton	7.00	@	9.00
Fuller's Earth, powdered.....C.	80	@	85
Green Vitriol (bulk).....C.	55	@	60
Hydrochloric Acid (18°).....C.	1.15	@	1.55
Iodine (resublimed).....Lb.	3.05	@	3.10
Lead Nitrate.....Lb.	8 1/8	@	8 1/4
Lithium Carbonate.....Lb.	65	@	70
Magnesite (raw).....Ton	7.50	@	8.50
Nitric Acid, 36°.....Lb.	3 7/8	@	4 1/4
Phosphorus.....Lb.	35	@	90
Phosphoric Acid, sp. gr. 1.75.....Lb.	21 1/2	@	25 1/2
Plaster of Paris.....Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....Lb.	6 1/4	@	7
Potassium Bromide.....Lb.	39	@	40
Potassium Chlorate, crystals.....Lb.	9	@	10 1/2
Potassium Cyanide (bulk) 98-99%.....Lb.	19	@	24
Potassium Iodide (bulk).....Lb.	2.60	@	2.65
Potassium Nitrate (crude).....Lb.	5	@	—
Potassium Permanganate (bulk).....Lb.	9 3/4	@	11

Quicksilver, Flask.....	39.00	@	40.00
Salt Cake (glass-makers').....C.	55	@	65
Silver Nitrate.....Oz.	36 3/4	@	38 1/4
Soapstone in bags.....Ton	10.00	@	12.00
Sodium Acetate.....Lb.	4	@	4 1/2
Sodium Bicarbonate (English).....Lb.	2 3/4	@	3
Sodium Bichromate.....Lb.	5	@	5 1/2
Sodium Chlorate.....Lb.	8 1/4	@	9 1/2
Sodium Hydroxide, 60 per cent.....C.	1.60	@	1.65
Sodium Hyposulfite.....C.	1.30	@	1.60
Sodium Nitrate, 95 per cent., spot.....C.	2.62 1/2	@	—
Sodium Silicate (liquid).....C.	65	@	1.50
Strontium Nitrate.....Lb.	6 7/8	@	7 3/8
Sulfur, Flowers (sublimed).....C.	2.20	@	2.60
Sulfur, Roll.....C.	1.85	@	2.15
Sulfuric Acid, 60° B.....C.	85	@	1.00
Talc (American).....Ton	15.00	@	20.00
Terra Alba (American), No. 1.....C.	75	@	80
Tin Bichloride (50°).....Lb.	14 1/4	@	14 1/2
Tin Oxide.....Lb.	51	@	53
Zinc Chloride (granulated).....Lb.	4 1/2	@	5
Zinc Sulfate.....Lb.	2 1/2	@	2 3/4

OILS, WAXES, ETC.

Beeswax (pure white).....Lb.	42	@	45
Black Mineral Oil, 29 gravity.....Gal.	13 1/2	@	14
Castor Oil (No. 3).....Lb.	9 1/2	@	10 1/2
Ceresin (yellow).....Lb.	12	@	22
Corn Oil.....C.	5.80	@	5.85
Cottonseed Oil (crude), f. o. b. mill.....Gal.	39	@	40
Cylinder Oil (light, filtered).....Gal.	21 1/2	@	32
Japan Wax.....Lb.	9 3/4	@	10
Lard Oil (prime winter).....Gal.	90	@	95
Linseed Oil (double-boiled).....Gal.	46	@	48
Paraffine (crude 120 & 122 m. p.).....Lb.	3 1/2	@	3 1/4
Paraffine Oil (high viscosity).....Gal.	26	@	28
Rosin Oil (first run).....Gal.	36	@	38
Sperm Oil (bleached winter), 38°.....Gal.	72	@	74
Spindle Oil, No. 200.....Gal.	18	@	19
Stearic Acid (double-pressed).....Lb.	9 1/4	@	9 3/4
Tallow (acidless).....Gal.	64	@	67
Tar Oil (distilled).....Gal.	30	@	31

METALS

Aluminum (No. 1 ingots).....Lb.	25 1/2	@	26
Antimony (Hallet's).....Lb.	8 3/8	@	9
Bismuth (New York).....Lb.	2.10	@	2.15
Copper (electrolytic).....Lb.	14 7/8	@	15
Copper (lake).....Lb.	15	@	15 1/4
Lead, N. Y.....Lb.	4.35	@	4.40
Nickel.....Lb.	50	@	55
Platinum (refined).....Oz.	46.00	@	—
Silver.....Oz.	56 7/8	@	57
Tin.....Lb.	46 1/4	@	—
Zinc.....Lb.	6.35	@	6.40

FERTILIZER MATERIALS

Ammonium Sulfate.....C.	3.23	@	3.25
Blood, dried.....Unit	2.85	@	—
Bone, 4 1/2 and 50, ground, raw.....Ton	28.50	@	—
Castor meal.....Unit	nominal		
Fish Scrap, domestic, dried.....Unit	nominal		
Mowrah meal.....Ton	9.00	@	—
Tankage, high-grade.....Unit	2.75	@	10
Phosphate, acid, 16 per cent. bulk.....Ton	7.00	@	8.00
Phosphate rock; f. o. b. mine:			
Florida land pebble, 68 per cent.....Ton	3.00	@	3.25
Tennessee, 70-80 per cent.....Ton	5.00	@	5.50
Potassium, "muriate," basis 80%.....Ton	38.55	@	—
Pyrites, furnace size, imported.....Unit	0.13 1/3		

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

MAY, 1913

No. 5

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, Wm. McMurtrie, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly.

Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

No claims will be allowed unless made within 60 days

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:		The "Rhenania" Steam Meter.....	423	
The Uranium and Radium Situation.....		356	The Official Tonnage Report of the Steel Corporation for 1912.....	424
Some Developments of the Iron and Steel Industry.....		357	The Status of the Chemical Industry of Austria-Hungary.....	424
ORIGINAL PAPERS:			The Foreign Metal Trade of the United States in 1912.....	424
An Electrolytic Method for the Prevention of the Corrosion of Iron and Steel. By J. K. Clement and L. V. Walker.....		361	Further Investigations for Securing Sound Steel Ingots.....	424
Paint as an Engineering Material. By Maximilian Toch		366	The "Optimus Plastic Alloy".....	425
Control of Initial Setting Time of Portland Cement. By E. E. Ware.....		369	"Ajax Anti-rust Sheets".....	425
Tests to Determine the Commercial Value of Wood Preservatives. A Progress Report. By Howard F. Weiss.....		372	The Painting of Steel Passenger Coaches.....	425
The Menhaden Industry. By J. W. Turrentine.....		378	The "Dissipator".....	425
Some Analyses of Fish Scrap. By J. R. Lindemuth and E. G. Parker.....		388	Recovery of Coke from Ashes.....	425
The Effect of Temperature, Acid Concentration and Time on the Bromination of Phenol for Quantitative Determinations. By L. V. Redman, A. J. Weith and F. P. Brock.....		389	The Production of Florida Phosphate in 1912.....	425
Petroleum Analytical Methods. By S. P. Sadtler.....		393	The Production of Cyanamide.....	426
Evaporation Test for Mineral Lubricating and Transformer Oils. By C. E. Waters.....		394	The "Fitting-Injector Dea".....	426
Preliminary Note on a New Method for the Direct Determination of Rubber. By L. G. Wesson.....		398	Electrolysis from Stray Electric Currents.....	426
Rapid Determination of Sulfur in Pyrites Cinder. By A. B. Conner.....		399	Standards for Hygienic Purity of Public Water Supplies.....	426
A New Technical Method of Spelter Analysis. By Eric John Ericson.....		401	Standards for Sewage and Sewage Effluents.....	427
Factory Method for the Determination of Total Fatty Acids in Cotton-seed Foots. By F. N. Smalley.....		402	"Hardened" Oils.....	427
The Modified Babcock for Fat in Sweetened Dairy Products—Ice Cream. By J. O. Halverson.....		403	Water Gas Tar as a Wood Preservative.....	427
Sampling Ice Cream. By J. O. Halverson.....		409	Pulp and Other Products from Waste Resinous Woods.....	427
Some Effects of Feeds upon the Properties of Lards. II. By C. L. Hare.....		410	The Effects of Tar Roads upon Vegetation and Animals.....	428
Fertilization of Citrus Soils. By Alfred Smith and H. E. Billings.....		415	Pressure Filters for Clarifying Trade Wastes.....	428
The Effect of Ignition on the Solubility of Soil Phosphates. By G. S. Fraps.....		416	The Hammond Water Meter.....	428
LABORATORY AND PLANT:			SCIENTIFIC SOCIETIES:	
Apparatus for the Precipitation of Barium Sulfate under Unvarying Conditions. By H. G. Smith.....		416	The Official Closing of the Eighth International Congress.....	429
An Adapted Wiley Extractor for Rubber Extractions. By Charles P. Fox.....		417	The United States Pharmacopoeia—The Progress of the Ninth Revision.....	429
ADDRESSES:			Division of Industrial Chemists and Chemical Engineers, American Chemical Society.....	430
Comments on the Report of the Investigation of the United States Patent Office. By L. H. Backeland.....		417	Division of Fertilizer Chemistry. American Chemical Society.....	431
The Plasticity of Clay. By John Stewart.....		421	Report of Committee on Potash. Fertilizer Division. American Chemical Society.....	431
CURRENT INDUSTRIAL NEWS:			Research Fund, American Electrochemical Society.....	432
The Tinning Industry.....		423	OBITUARIES:	
Linseed Oil.....		423	Dr. Friedrich W. C. Schniewind.....	432
			NOTES AND CORRESPONDENCE:	
			Lead Poisoning.....	434
			The American Alcohol Insoluble Test for Shellac.....	435
			Production of Camphor in Japan.....	436
			Mineral Production of Canada.....	436
			Waters of the Breitenbush Hot Springs, Oregon—A Correction.....	436
			BOOK REVIEWS:	
			Utilization of Atmospheric Nitrogen; Proceedings of the American Gas Institute; Treatise on General and Industrial Inorganic Chemistry.....	437
			NEW PUBLICATIONS:	439
			RECENT INVENTIONS:	440
			MARKET REPORT.	442

EDITORIALS

THE URANIUM AND RADIUM SITUATION

Some months since, rumors reached the U. S. Bureau of Mines of an increased demand for carnotite ores from Colorado and that these ores were being shipped abroad in some quantity. Further, it was reported that the methods of production involved large losses of material and that methods for concentrating low-grade material now being thrown on the dump were greatly needed. Accordingly, Messrs. R. B. Moore and K. L. Kithil were assigned to the task of investigating the situation with headquarters at Denver, where the Bureau established a laboratory for the purpose of investigating the rarer metals occurring in the western part of the United States and problems bearing upon the prevention of waste and increased efficiency in the mining industry. The surprising conclusion has been reached that while all the radium placed upon the market in the last few years has been produced in Europe, a large portion of this output has come from American ores.

Radium institutes have been established in Austria, France, Germany and England, a European science and industry have been developed from American radium ores and even the uranium present with the radium has been manufactured into marketable condition only in foreign countries and returned in finished condition to our own. American hospitals and physicians have been forced to procure from abroad such radium as they could afford for experimental purposes, and investigations in our governmental and university laboratories of the wonderful properties of radium and their possible application to the eradication of disease and the development of industry have been hampered by the almost prohibitive prices at which the finished material is held.

While the Austrian government, realizing the untold possibilities of the radium ores of St. Joachimsthal, has purchased the mines, put their output under direct governmental supervision, and has entered into an arrangement whereby this ore is worked up in coöperation with the Vienna Academy of Sciences for experimental purposes in a carefully administered radium institute, America has allowed her large and much greater resources to be exploited on a basis which wastes perhaps irretrievably a large portion of the material mined, and has exported carefully selected ores at a price by no means commensurate with their radium value if worked up at home.

Even before carnotite was exported, pitchblende of the highest grade was sent out of the country at a time when the world's radium output was supposed to be coming from Austrian ores. At least 20-25 tons of high-grade pitchblende have been sent out of the country. Within the last two years, however, foreigners have realized the value of our carnotite resources, and most of the radium that has been exported has gone abroad in this ore.

During the last year, carnotite was produced carrying 28.8 tons of U_3O_8 , from which 8.8 grams of radium chloride or 11.43 grams of radium bromide could be obtained. Practically all of this ore was shipped abroad for the extraction of radium. The value of the radium salts extracted would be \$528,000 at the minimum market price. The total supply of radium salts from all other sources including the Austrian mines was probably not more than 3.65 grams of radium chloride, basing the production of the Austrian mines for 1912 upon that of 1911 which is known.

Pitchblende, the richest of all uranium minerals is composed mainly of uranium oxide but also carries lesser quantities of a large number of other substances. It has been found in small quantities in Connecticut and in the feldspar quarries of North Carolina. Practically the total American output has come from the mines in Quartz Hill, Gilpin County, Colorado. The mineral is a heavy, black substance which can be readily identified by any one by suspending a sample of the pitchblende above a photographic plate wrapped in black paper and kept in the dark for a few days with a key or other metal object opaque to radium radiations placed between the sample of ore and the plate so that when the plate is developed a shadow-graph will identify the ore. Pitchblende may carry as high as 80 per cent. uranium oxide, although the average ore is not nearly so rich.

Carnotite is a yellow mineral consisting mainly of potassium uranyl vanadate but containing also small amounts of barium and calcium compounds. Being a uranium mineral, as is pitchblende, it of necessity carries radium, although it has not yet been definitely established that the uranium and radium are in equilibrium as they are in pitchblende. However, it is known that in our western carnotite the amount of radium is not far from the equilibrium ratio and in the calculations given above an allowance of 10 per cent. has been made to cover this possible deficiency.

While carnotite is known to occur in smaller quantities in other states, the more important deposits are scattered over a considerable area in Colorado and Utah, embracing Meeker and Skull Creek, Colo., Green River, Thompson's, Moab, Richardson, Table Mountain, Pahreah, and other places in Utah. The largest proportion of the ore, however, has been produced in or around Paradox Valley in southwest Colorado, from which it has to stand long hauls by pack animal or wagon to the railroad. Carnotite always carries vanadium as well as uranium and radium but is purchased almost wholly on its radium content, comparatively little being allowed for the vanadium present.

The ore, consisting of a fine-grained sandstone containing yellow finely pulverulent carnotite, occurs

in pockets and is easily mined. As ore below 2 per cent. uranium oxide cannot at the present time find a market, a considerable portion of the ore has been thrown on the dump and is now being wasted, as material of lower grade has to be discarded on account of the long haul and the fact that European buyers have set this standard as to quality. Ores of higher grade are sometimes obtained but they occur only in small pockets and it is generally advisable to mix these high-grade ores with ores of somewhat lower content in order to increase the marketable output. Ore of 2 per cent. uranium oxide is now worth approximately \$75 per ton f. o. b. New York. In the mining of these carnotite ores, it is probable that 5 tons of material capable of concentration are thrown upon the dump for every ton that finds its way to market. To develop methods for concentration of these ores and save the valuable material now wasted is one of the problems before the Bureau of Mines with fair prospect of a successful conclusion.

It is difficult to estimate the total amount of radium that has been produced up to the present time, but it is quite certain that if the ores which have been mined in this country and abroad and sold for radium production have been actually worked up into this material, there is now in existence something like 40 grams ($1\frac{1}{4}$ ounces) of radium. The price of radium salts varies somewhat. In large quantities it has been \$60,000 per gram for both radium chloride and radium bromide, although the latter contains less metallic radium in proportion to its weight than the former. It should be remembered, therefore, that it is more advantageous to purchase radium chloride than radium bromide. In small quantities the average price has been \$80,000 per gram which represents about \$2,250,000 an ounce.

The figures given show very plainly that the United States has taken the palm from Austria as the radium-producing country of the world. Very few people have been cognizant of the fact that the United States has such deposits within her borders. Up to the present time very little interest has been taken in the matter, and only one firm has engaged in the extraction and refining of radium in this country—a condition which is deplorable. This firm has not yet entered the radium market.

Practically every ton of ore mined in 1912 went abroad, and as the American deposits are far from being inexhaustible we are rapidly depleting our own reserve and are shipping from the country material which cannot be replaced and which is of great value and of unknown possibilities.

The applications of radium are still too little understood to admit of definite statement. Its discovery and marvelous properties have already changed our ideas regarding the constitution of matter, and scientific investigation will undoubtedly lead to valuable results which we cannot now even foresee. Altogether too many incorrect statements and vague speculations have been placed before the public as

to its use in medicine. A recent report of the London Radium Institute and the many articles emanating from minor laboratories experimenting in the application of radium to therapeutics all tend to show, however, that it has a real value, the certain application of which must await further experimentation. In the meantime no credence should be given to the many stories that are sure to be printed, unless they are backed up by the highest medical authority which will always give publicity with caution. The best medical authorities appear to agree that, up to the present time, radium has not been proved to be a specific for any disease, although it has been shown to be helpful in many cases. The outlook for its future application to certain diseases not easily treated otherwise is decidedly encouraging.

Apparently no uranium is worked up in the United States, but according to statistics gathered by the division of mineral resources of the U. S. Geological Survey, about \$14,000 worth of its oxides and salts were imported into the United States in 1911. It is one of the few materials shipped abroad as ore and returned in manufactured form.

A preliminary report on uranium, radium and vanadium by R. B. Moore and K. L. Kithil will soon be issued by the Bureau of Mines. This bulletin describes the carnotite deposits of Colorado and Utah and the pitchblende deposits of the former State. It also contains detail, of which the foregoing is simply a general summary, which cannot fail to be of value to all those interested in our mineral resources and their development.

CHARLES L. PARSONS.¹

SOME DEVELOPMENTS OF THE IRON AND STEEL INDUSTRY

In this résumé of developments of an industry, only those points of more common interest or significance can hope to be touched and others of equal importance are doubtless overlooked. Only the peaks can be mentioned and these in general terms, for the most part. In general, progress in all industries synchronizes to a large extent and points here referred to correlate with some in other lines—each making possible reciprocal advances in the other.

Naturally, the subject of first importance is the ore supply. Doubtless since the beginning of iron making, the exhaustion of ore supplies has been the subject of serious consideration by some. The first exhaustive studies were those of the Swedish geologists, Tiberg in 1898 and Tornebohm in 1905. The latter's estimates indicated most serious depletion of resources within fifty years and with the most generous allowances for new discoveries, a serious condition faced the world in a half century, if the rapid growth of production was to continue. Without any analysis of his figures, it may be said that fortunately for

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913, by permission of the Director of the Bureau of Mines.

us and the future, new discoveries have more than kept pace with both current output and the rapid rate of increase in production, until the exhaustion of known reserves to-day is actually more years ahead of current consumption than ever before, even allowing for the geometric increase in production.

Since that time, the Giant Mesabi Range has not only grown in importance but its reserves have continually increased, until after producing nearly 300 million tons of ore, they are greater than at any time in its history and those whose opinion should be respected confidently assert that the end is not yet in the growth of its reserves. While this great deposit stands out in relief among all developed deposits, scarcely an important field has not added to its reserves somewhat proportionately. In America, the other Lake Superior Ranges have had their reserves extended enormously by search and development. Since these notes were made, a well known mining engineer, in reviewing the Lake Superior Region, makes the prediction, based on long and intimate familiarity with the entire region, that in the State of Michigan alone, more ore will yet be discovered than is now credited to the Mesabi—though the latter's present known reserves are ten times those of the State. In addition to enormous extensions of the older Lake Superior Regions, including the Mesabi, new areas have been followed up. The most fruitful so far is the Cuyuna Range, which has already uncovered an immense field.

After the Southern Appalachian field, the American deposit of third magnitude is the comparatively recently discovered one of Cuba in the northeast of Oriente Province, the easternmost of the Island. While Cuba has produced ores for many years, mainly from the southern coast of the same province, formerly Santiago de Cuba, this ore was of a different character, being a hard, massive hematite and magnetite, while the more recent discoveries are hydrous brown hematites. They are blanket formations of great extent and have this general resemblance to the Mesabi but are much shallower and entirely without overburden, so that steam shovel operations start at grass roots. Two general deposits have been thoroughly prospected, the Mayari on Nipe Bay, and the Moa ore body some fifty miles to the east. The former is developed to a very considerable extent and has been increasing its production for three or four years past. The average depth, as determined by very careful boring, is 18 feet, the limits being 12 to 40 feet and the deposit is estimated to contain six to eight hundred million tons. The Moa deposit has been estimated at about one billion tons, but little development has been done. A third ore body, known less thoroughly than the other two, has been estimated to contain three hundred million tons.

This Cuban ore possesses several unusual characteristics, both physically and chemically. It is of a clayey consistency due to a high percentage of alumina and some 25 per cent. of hygroscopic and about 11 per cent. of combined water. The water is removed at the mines to facilitate loading into boats and sub-

sequent handling, as well as the enormous reduction in freight. It carries from 1.5 to 2.0 per cent. chromium, approximately half as much nickel, and 8.0 to 12.0 per cent. alumina, presenting difficult metallurgical features for both the blast furnace and steel operations. A large tonnage of steel has been produced, in whole or part from the ore, as well as the pig iron being used to advantage for special foundry mixtures. In the metallurgical processes, the nickel is conserved and the chromium to some extent. With the increasing use of alloy steels, largely nickel and chromium, here would seem to be a natural deposit with both in proportions that could be well utilized, either alone or as a basis for mixtures, when both elements would be entirely conserved in the metal product.

The discovery of these later Cuban deposits surely suggests how far a cry is the exhaustion of the world's ore supply! Here was a region in which much general and detail prospecting had been done for years; the existence of some of the ore was known, but it was believed to be in such shallow deposits or of so low grade that no serious attention was given it for nearly a generation, and only after the most painstaking and exhaustive prospecting was the ore shown to be in sufficient volume to have immense commercial and economic importance. With the knowledge of the discoveries that have been made and the enormous extension of both merchantable ore in old regions and of low-grade deposits that have more than a potential value though efficient concentration methods, it is difficult, even allowing for the doubling of our consumption about every ten years, for most of us to sympathize with the past predictions of some economists—both commercial and geological.

While the above covers the three known American regions of preëminent importance, a number of other deposits are known and more or less developed, some of them among the older producing sections. In the past decade or two, magnetic concentration has grown until over a million tons are produced annually, mainly in New York. The washing of the lean or sandy ores of the Western Mesabi has grown until in the past year the production reached over three million tons of concentrates. This development has been in progress experimentally for a number of years but only within two or three has the production been appreciable. Towards the western end of the Mesabi Range the ore is interbedded with sand in such a manner that much of it cannot be separated in mining, and concentration is necessary. These sandy ores, of enormous extent, were generally considered of doubtful value in the earlier history of the Range, but have added enormously to Mesabi reserves in more recent years. Their comparatively recent utilization also serves as an illustration of the economic possibilities or other lean ores in the near future.

Another region remains to be mentioned. Within the past two or three years considerable attention has been attracted to the reported deposits of Brazil. The first accurate and exact general knowledge of the extent of the deposit was contributed to the

International Geological Congress of 1910 by Dr. Derby, of the Brazilian Geological Survey. Drs. C. K. Leith and E. C. Harder, in "Economic Geology," Vol. VI, 1911, describe a portion of the deposit and say: "Estimates of tonnage for the region as a whole would be premature with the present state of knowledge, but it is certain that the estimate of Dr. Derby for the International Congress, of two billion tons for the district, is conservative. Of the high-grade massive hematite and jacutinga ranging from 63 per cent. to 69 per cent. in iron, the tonnage is probably not far short of the total reserve of available ores in the Lake Superior region to-day. Individual deposits contain several hundred millions of tons"—"Single lenses are known which are more than three miles in length and range up to 2000 feet in thickness." This, too, is only a part of the known deposits of the district, to say nothing of other regions in the country that are known to contain large quantities but have not been examined in detail. Nor does it consider any but the high-grade ore and that of a single section, all of it of higher grade than most of our merchantable ores of the Lake Superior Region to-day.

Most of us had come to feel, perhaps unconsciously, that we had in the Lake Superior accumulation an exclusive possession—a sort of aristocracy of iron ore deposits—but here is a region whose high-grade ores (according to Dr. Leith and confirmed by others), in quality beginning where ours stop, alone are apparently equal to this whole region. And unless the deposit differs from all known large ones, in that the low-grade material is invariably greater in volume and actual iron than the high-grade portion, this would seem to be the greatest yet known. Yet as it is unusual in its richness and method of deposition, stated to be mainly direct sedimentation without secondary enrichment as the Lake Superior Region, it may also be unusual in its leanness, and Nature may have done so efficient a concentrating job that no tailings were left over.

The above necessarily fragmentary data are given, less for their specific value or interest, than for their suggestiveness and significance. For after all, much the smaller part of the earth has been thoroughly examined for iron and it seems not unreasonable that nature will be as generous in these regions as those more thoroughly explored, and will uncover supplies as economic demands develop, or in anticipation of them. But without any such trust in the future or Providence, present known supplies would seem to be ample to provide for an expanding consumption, previously doubling about every ten years, for a long way into the future—though the ore production and consumption gradient is flattening out. In 1890, in the United States, nearly four tons of ore were consumed to one ton of steel produced, ten years later 2.7 tons, and in 1910 2.1 tons, due largely to the growth of the open hearth process and the consequent utilization of scrap, though several other factors are involved.

All progress is conservation and the Iron and Steel Industry has availed itself of every advance that could be efficiently utilized—and efficiency in the

sense of a much larger problem than mere technical efficiency. The abundant use of by-products and low-grade materials, from the dressing of lean ores to the making of a large part of the Portland cement of the country from a by-product, together with utilization of many intermediate wastes, abundantly testifies to this. As a further expression of it, I quote from *Bull.* 47, p. 15, on "Mineral Wastes," of the United States Bureau of Mines, as follows: "The Metallurgy of iron has reached a perfection beyond that of any other metal and wastes have been eliminated to an extent that serves as some indication of what perhaps may be done in other industries when the same intelligent investigation has been applied." Such a statement from so authoritative a source on conservation problems should be gratifying to any industry, but the most promising feature in this one is the activity in utilizing additional by-products so that the saving of wastes may be said to be only fairly started in many branches of the industry.

In fuel, the by-product coke oven is making pronounced progress but less rapidly than could be hoped for. It would seem that it is on the point of a rapid extension as the present coke production is not only short of immediate demands, but with the normal expansion of iron production the existing coke capacity cannot supply it, so that logically extensions should come through by-product ovens. The growth of the retort oven has been retarded, among other reasons, by an unsatisfactory market for some of the by-products, more especially for tar. Tar was first used in America as open hearth fuel at Sydney, N. S., in 1904 (*Iron and Steel Magazine*, Jan., 1904). While the use of tar as a metallurgical fuel is a base one to the Chemist in view of its possibilities, yet it is surely a more worthy one than roof and road making. This application promises to be of some influence as a factor in retort oven extension as even relatively small increments of advantage now count for much. Taking the figures of the U. S. Geological Survey, the average coal, in the amount necessary to produce the coke for one ton of pig iron, will yield, as tar, approximately 25 to 30 per cent. of the fuel necessary to convert the ton of pig iron into steel in the open hearth furnace—which makes it of no small consequence—its commercial value, of course, depending on the cost of other fuel to do the same work and the price of tar for other uses.

In connection with the blast furnace, application of the dry blast has not become so general as was anticipated a few years ago. Several thin lined furnaces, following a rather common German practice, have been built and much is claimed by their advocates. In connection with the problem of dust removal for both gas engine and fuel purposes, while accomplished satisfactorily, more efficient schemes are being sought. The Cottrell process has been proposed for blast furnace gas and may soon be applied experimentally. The turbine blower has been installed at several plants and many believe it will quite extensively replace reciprocating blowers.

In steel-making processes perhaps the greatest

activity is in evidence and it is difficult to restrict references. The striking change is the familiar transition from Bessemer to open hearth, which has been in progress for the past decade or more. In 1900, 66 per cent. of the product was Bessemer and 33 per cent. open hearth, while in 1911 the proportions were exactly reversed. The tendency is strongly in the same direction and the once mighty process will soon play a relatively insignificant part as a complete process in our American production—unless present tendencies take a radical turn. The most important phase of an extended life for the Bessemer seems to be as an auxiliary of the open hearth—possibly of the electric furnace. The extensions of the Bessemer-Open Hearth duplex process have been marked until seven or eight large American plants are duplexing all or part of their product (or are about ready to), with the probability that the number will be increased rather than diminished. In one instance basic-lined vessels are used. But in the duplex process, the Bessemer becomes the servant, the auxiliary of the more powerful Open Hearth, and is no longer a complete process where duplexing is regularly done.

The chief reason for this development is the greatly increased production possible from a given open hearth unit. Under the best conditions, the open hearth time is less than half, and some claim it should be only one-third the regular time. It is probably conservative to say it more than doubles the capacity of an open hearth plant. Some companies plan to operate duplex under stress of production, and straight open hearth at other times, making a flexible arrangement to meet fluctuating demands, with much less investment in plant for a given output. In operating the duplex process, the pig metal is partially blown in the converter, removing the silicon, manganese and as much of the carbon as desired, and successive charges of partially blown metal are transferred to the open hearth furnace where the final purification is effected.

In the open hearth process proper, developments are naturally the most active. The increased size of single units to over 100 tons for stationary furnaces where but a few years back 50 tons was regarded as large, and to 250 tons for tilting furnaces has been limited in the case of the stationary furnace only by the handling apparatus—ladle cranes.

While important work is being done in many directions, the heat problem is the one receiving most attention in studies of economies of initial fuel and better utilization of waste heat. An early attempt of Siemens in attaching the producer directly to the furnace is finding expression and extension of the same idea in the use of powdered coal and the entire elimination of the producer. Furnaces have been operated experimentally but no records are known of furnaces that have run for any considerable length of time on powdered coal. The stack losses in sensible heat in the open hearth are enormous, and much effort is being directed toward their more efficient saving, at present by the use of waste heat boilers.

The electric furnace has been a commercial apparatus

in the steel industry now for a number of years and much extension has resulted. Its chief applications, however, are under special conditions or for special products. It was anticipated that by this time it would be a factor in tonnage production as complementary to either the Bessemer or Open Hearth. The most promising field seems to be in displacing the crucible process and for the making of special and alloy steels in general. It finds considerable application in Europe for melting alloying additions in larger operations, and offers many advantages over other apparatus for this purpose owing to the non-oxidizing atmosphere. Probably it will first establish itself here in connection with large operations. Another suggestion, by Dr. J. W. Richards, is the use of the electric furnace as a receptacle after the steel has been made—or as a holding ladle—so that occluded slag and oxides may have time to separate. It looks to the writer as if the electric furnace would first gain a secure foothold in the larger tonnage operations as an adjunct, as indicated above, most likely for melting additions, or for holding the product of other processes for final elimination of certain contaminations, though the latter seems more remote.

Perhaps the chief spectre of the steel-making end of the industry has always been the ever present pipe in the ingot which still remains and its successful prevention is yet a "pipe" dream. However, progress is evident and much experimental work has been done and is in progress. Advances have been made in the careful attention to many details of manufacture and refinement and modification of methods of alleviation that have long been proposed—such as various methods of keeping the ingot open so that the top does not freeze ahead of the remainder of the mass; the use of thermit cartridges for the same purpose and other means of keeping a hot top; fluid compression has been used for many years but has never been developed for general application. A recent attempt, or revival of an earlier one, is that of rolling the ingot before complete solidification—the walls being frozen and the interior liquid or plastic, so that the interior cavity may be closed. Heavy cropping is universal where the pipe seriously affects product, so that while prevention has not yet been reached, a successful cure is now generally applied where necessary.

The development of alloy steels—for our purpose confining alloy steels to material used for construction purposes and not crucible or tool steels—has been extensive. The largest use is probably that of nickel and chrome, separately or together, with or without vanadium. The extensive use of vanadium steels is well known and the effect of this element is one of the most interesting of any addition. Aluminum has long been used and titanium more recently, but as generally used, they are not alloys but merely scavengers, leaving practically no trace of their presence. A more recent alloying addition is copper, particularly for certain classes of sheets, although used in some other products. Its chief advantage is as an inhibitor of corrosion and quite a number of sheet steel manufacturers make copper-bearing steels. An

interesting point in this connection was the former universal condemnation of copper by steel-makers as a producer of red shortness but in very considerable amounts its effect is not now feared in this respect.

A development, or an extension of one originating in the industry itself, or with workers associated with iron and steel investigation, is that of heat treatment, which is more largely applied by fabricators of steel parts, especially of high-grade machine parts for automobiles, engines and many forms of apparatus where high duty is requisite. The ubiquitous automobile has contributed more to the extension and application of heat treatment than any other factor. Not that discoveries have come from this source, but in their aggressive and enterprising spirit the builders have availed themselves of every possible advance in applied science to perfect details of construction and quickly recognized the benefits of the proper heat treatment of steel. In this way, the automobile industry has accelerated the application of heat treatment more than any other agency until now every progressive maker of parts for high duty

service in many lines of construction, gives great attention to this feature. The proper heat treatment of steel has added greatly to the safety and reliability of much of our modern equipment in various lines and it is difficult to imagine how much of the exacting service could otherwise have been met.

No survey of progress, however brief, should neglect the human side of the industry—the efforts for betterment, and accomplishments in this direction. While efforts of this kind are not distinctive of any industry but represent a movement of the period in all lines, no branch of industry has more vigorously promoted or is more successfully advancing this work than the one under consideration. The work for sanitation, safety and health is of amazing magnitude, practically every concern, not only generously spending money, but what is more important, conscientiously working to conserve the health, safety and welfare of all classes of employees until no finer examples of results exist in our industrial life than many that are to be found in the Iron and Steel Industry.

G. D. CHAMBERLAIN.

ORIGINAL PAPERS

AN ELECTROLYTIC METHOD FOR THE PREVENTION OF THE CORROSION OF IRON AND STEEL¹

By J. K. CLEMENT AND L. V. WALKER

INTRODUCTION

According to the electrolytic theory of corrosion, when iron is oxidized in the wet way it first goes into solution as ferrous ions. The ferrous ions are then oxidized by the oxygen present in the water to ferric ions and precipitated as ferric hydroxide. Simultaneously with the formation of ferrous ions, hydrogen is liberated on the surface of the iron. The passage of the iron from the atomic to the ionic state and the passage of the hydrogen from the ionic to the atomic state are accompanied by a transfer of electricity. The ferrous ions derive from the metal surface a charge of positive electricity, the hydrogen ions give up a charge of positive electricity and a current flows through the metal from the point where hydrogen is liberated to the point where iron is dissolved.

If iron and a metal having a greater "solution tension" than iron—for example, zinc—be immersed in an acid solution and connected externally, through a wire, zinc will go into solution, hydrogen ions will be liberated on the iron, and current will flow through the wire from iron to zinc. The potential difference between zinc and iron being opposed to the potential difference between iron and electrolyte, neutralizes the force required to pull the positively charged iron ions away from the negatively charged surface of the iron electrode. Consequently iron does not go into solution.

In place of zinc, other conducting materials—for example, carbon—may be used as the anode, and the E. M. F. required may be furnished from an external source.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

In this way electric energy derived from either a battery or a generator may be used to protect metals from corrosion under water.

A vast amount of work, both theoretical and experimental, has been directed to the study of the causes of corrosion and the development of methods for its prevention, and the literature on the subject is extensive.² Very little attention, however, seems to have been given to the development of an electrolytic method for the prevention of corrosion. An electrolytic method has been used to some extent for the protection of boilers.³ This method consists in submerging a bar of zinc in the boiler water and connecting the zinc electrically with the boiler plates. After the experiments described in this paper were begun it was found that an electrolytic process for the protection of metals had been patented by an Australian inventor.⁴ The writers have been unable to find any data published by the inventor.

In a paper presented before the Sydney, Australia, Section of the Society of Chemical Industry, G. Harker⁵ describes experiments on the prevention of the corrosion of iron by electrolysis. He determined the current density necessary to prevent the corrosion of steel plates submerged in $N/25$ H_2SO_4 , tap water, sea water and "dilute acid." The results of Harker's experiments, which furnish the only data on the sub-

¹ Author's abstract of an address delivered as chairman of the Pittsburgh Section of the American Chemical Society, January, 1913.

² Cushman, A. S., and Gardner, H. A., "Corrosion and Preservation of Iron and Steel," New York, McGraw-Hill, 1910. "List of References to Books and Magazine Articles on Metal Corrosion and Protection," Bulletin, Carnegie Library of Pittsburgh, July, 1909.

³ J. H. Paul: "Corrosion in Steam Boilers," *Trans. Soc. Engineers*, **31**, 147.

⁴ See *Elec. Review and West. Electn.*, **58**, 326 (1911).

⁵ G. Harker and J. McNamara, "Electrolysis as a Means of Preventing the Corrosion of Iron and Steel," *Jour. Soc. Chem. Ind.*, **29**, 1286 (1911).

ject which the writers have been able to find, will be discussed in connection with the results of their own experiments.

EXPERIMENTS BY F. M. STANTON

Experiments to devise an electrical method for the prevention of the corrosion of steel immersed in acid water were undertaken at the Pittsburgh Experiment Station of the Bureau of Mines, in May, 1911, by Mr. F. M. Stanton.

Stanton's work included laboratory experiments and tests on plates immersed in the Monongahela River. In the laboratory experiments, steel plates 6 mm. \times 19 mm. \times 51 mm. were suspended in separate vessels in $N/5$ H_2SO_4 . In one vessel a carbon rod was suspended near the steel plate and connected to the positive pole of a storage battery, the negative pole of which was connected with the steel plate. In the second vessel the steel plate was not protected. After 24 hours exposure it was found that the unprotected plate had lost in weight 1.8100 grams and the protected plate only 0.0012 gram.

In the tests with plates submerged in the Monongahela river a much smaller current density was used than in the laboratory experiment, and the protection against corrosion was much less complete. The plates used in these tests had the following dimensions: 6" \times 8" \times 1/8". The protecting current was furnished by a 2-volt accumulator. The loss in weight of the two plates at the end of fifteen days immersion was for the protected plate 0.7 gram and for the unprotected plate 10.9 grams.

EXPERIMENTS TO DETERMINE CURRENT DENSITY REQUIRED TO PREVENT CORROSION

Mr. Stanton left the service of the Bureau in July, 1911, and the work was interrupted until December,

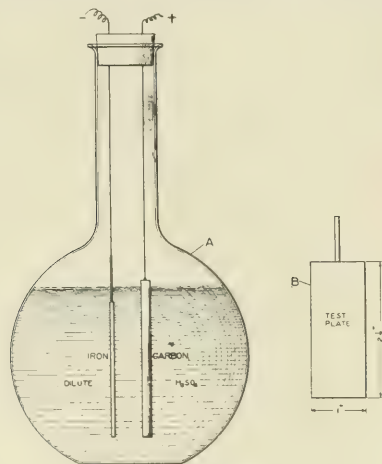


FIG. 1—APPARATUS I

1911, when experiments were resumed by the authors and Mr. A. E. Hall.

The object of the experiments to be described was to determine the current density required to prevent, under various conditions, the corrosion of steel plates in acid water.

EXPERIMENTS WITH APPARATUS I.—The first method of determining the protective effect of small currents was to suspend an iron plate, of the dimensions shown in Fig. 1, in an 800 c.c. flask parallel to a 1/4 inch carbon rod and 1/2 inch from it. Using storage batteries as a source of E. M. F., a current was passed from the carbon rod through dilute sulfuric acid to the iron plate. The current regulation was accomplished by the use of variable resistances and the current measured by the drop in potential over a known resistance, by means of a Siemens and Halske millivolt meter; electrical connections were always completed before any acid was introduced into the flask and the current was regulated immediately thereafter. In order to save time six such flasks were used in each experiment.

The results of the first series of experiments are shown graphically in Figs. 2 and 3. The experiments represented by the curves in Fig. 3 were made

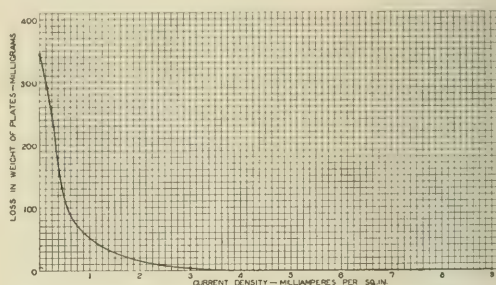


FIG. 2—RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY Apparatus I. Duration of Test, 45 hrs. $N/5$ H_2SO_4 , Electrolyte Unstirred

under uniform conditions, except that the duration of the test was varied. These experiments indicate that a certain definite current density must be main-

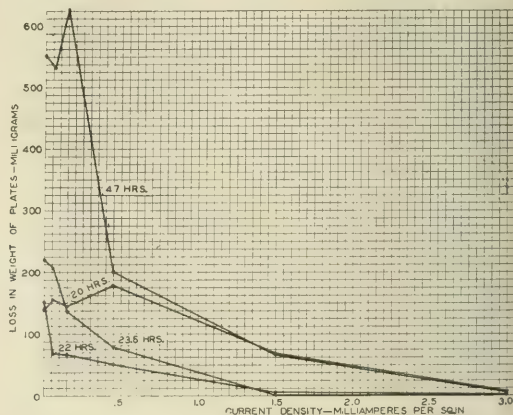


FIG. 3—RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY Apparatus I. $N/10$ H_2SO_4 , Electrolyte Unstirred

tained in order to reduce the corrosion loss to a minimum. On account of the poor agreement between the results of individual experiments, a second type of apparatus was designed.

EXPERIMENTS WITH APPARATUS II.—In order to

eliminate as fast as possible any error due to differences in acid concentrations about the iron plates, all the test plates were immersed in a common vessel. Another improvement was the employment of an acid reservoir, and a constant level device by means of which fresh acid could be fed into the containing vessel at any desired speed, and the excess electrolyte could be siphoned off through the level bottle into the overflow. The vessel was a porcelain-lined cylindrical dish of about 2250 c.c. capacity and the plates were supported by a thin wooden cover at points on a circle 4" in diameter, and at whose center the carbon rod anode was suspended. The plates were set equi-distant from each other and, of course, from the anode.

Six experiments were conducted according to this scheme and the acidity of the electrolyte, was determined at the end of each run. There was always a

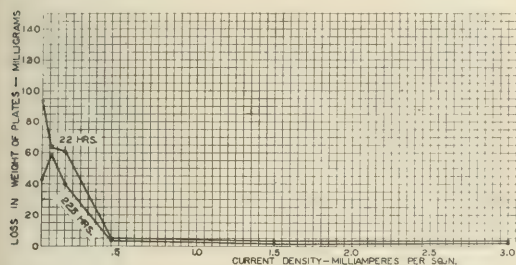


FIG. 4—RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY Apparatus II. $N/10$ H_2SO_4 , Electrolyte Unstirred

considerable decrease in acid strength which could be eliminated to a large degree by increasing the rate at which the acid was fed. For example, at the end of a 27-hour run, started with $N/10$ H_2SO_4 , the acidity was 85/1000 normal. As all the plates, however, were subjected to the same variation in the strength of the electrolyte, the loss in weight of the plates should be comparable.

The curves in Fig. 4 represent the plate losses for experiments 11 and 12, in which apparatus II was used. Though the results do not check exactly, they are more consistent than those of the previous experiments. The indications from the experiments of Series I and II are that a current of 0.4 milliampere per square inch (figuring $2/3$ of the back of the plate as is customary) will prevent 93 to 94 per cent. of the corrosive action of $N/10$ H_2SO_4 when the solution is not stirred.

EXPERIMENTS WITH APPARATUS III. — Apparatus III, the one finally adopted, is shown in Fig. 5. It differs from apparatus II chiefly in having a greater capacity—4.5 liters—and in being provided with an attachment for stirring the electrolyte. The plates were arranged as before, except that they were set $2\frac{1}{2}$ inches from the carbon rod, instead of 2 inches, in order to keep them under water when the electrolyte was rotating rapidly. For stirring, a low power, hot air engine gave fairly constant speed and could be run over night. In order to be able to calculate the current densities with greater accuracy, all surfaces of the

plates except the one facing the anode were protected by being painted with Bakelite Lacquer. An application of four or five coats gave a good, smooth surface that was impenetrable by acids.

The first few experiments using the final apparatus

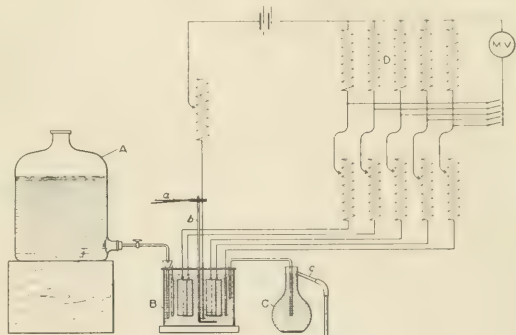


FIG. 5—APPARATUS III

A, acid reservoir; B, electrolytic tank; C, level bottle; D, known resistance; a, belt to motor; b, stirrer; c, to overflow

were run with the stirrer rotating at 660 R. P. M. and under these conditions, currents that had protected the iron plates almost completely in still water, were absolutely useless. On reducing the stirring rate to 35 R. P. M. in $N/100$ acid, small currents were again effective, and runs could be checked with a fair degree of accuracy.

Fig. 6 shows the results of experiments using $N/100$ H_2SO_4 as electrolyte and with the stirrer running at 35 to 40 revolutions per minute. In this series of experiments the electrodes were removed from the electrolyte at frequent intervals and their loss in weight determined. The curves in Fig. 6 show that the plates having a current density of 0.4 milliampere

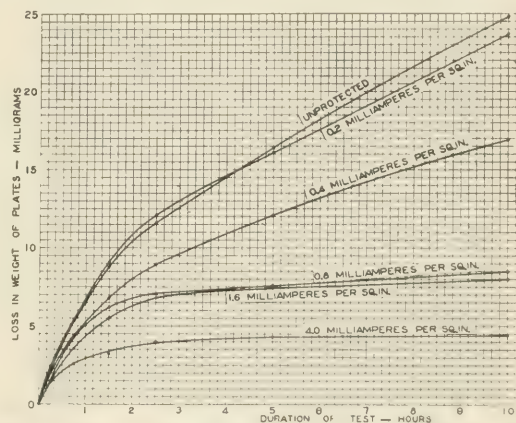


FIG. 6—EFFECT OF CURRENT DENSITY ON RELATION BETWEEN LOSS OF WEIGHT AND DURATION OF TEST Apparatus III. $N/100$ H_2SO_4 , Electrolyte Stirred, 35 R. P. M.

per square inch or less, continued to lose weight during the entire period of the experiments. Plates protected by current densities greater than 0.4 milliampere per square inch exhibited a marked initial corrosion and thereafter no further loss in weight.

The initial loss in weight of the plates protected by current densities greater than 0.4 milli-ampere is probably due to the fact that at the start of the experiment the plates were covered by a film of air and that the oxygen of the air film acted as a depolarizer. Some time elapsed, therefore, before the plates became completely polarized, and during this period they were incompletely protected by the current. The difference between the rate of loss in weight of the unprotected plate during the initial period and the rate of loss during the remainder of the experiment is probably due to a difference between the structure of the original surface of the metal and the interior, as well as to the action of the film of air surrounding it at the beginning of the experiment.

EFFECT OF PASSING OXYGEN THROUGH ELECTROLYTE.—On account of the depolarizing effect of oxygen it was to be expected that the amount of oxygen present in the electrolyte would be an important factor in determining the speed of corrosion. Fig. 7 shows the results of a series of four experiments made to ascertain the effect of increasing the amount of oxygen in the electrolyte. The composition of the electrolyte, $N/100 \text{ H}_2\text{SO}_4$, and the

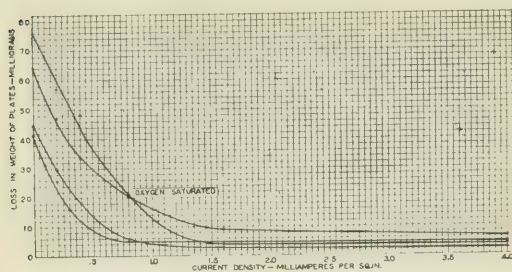


FIG. 7—EFFECT OF OXYGEN ON RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY
Apparatus III. Duration of Test, 24 Hrs. $N/100 \text{ H}_2\text{SO}_4$, Electrolyte Stirred, 35 R. P. M.

speed of the stirrer, 35 R. P. M., were the same in all four experiments. The lower curves represent two experiments with the usual amount of oxygen present. The electrolyte was prepared by adding sulphuric acid to distilled water without any special precautions to exclude the air or to aerate the solution. In experiments 38 and 39, represented by the two upper curves of Fig. 7, the electrolyte was saturated with oxygen by rapidly bubbling oxygen through it during the experiment. The curves show that increasing the amount of oxygen in the solution accelerates the speed of corrosion very materially, the loss of weight in 24 hours being about twice as great when oxygen was passed through the electrolyte as when oxygen is supplied by diffusion only. It follows from this that the rate of corrosion in any acid solution depends on the degree of aeration of the solution.

EFFECT OF STIRRING.—The enormous acceleration of corrosion produced by extremely rapid stirring, 660 R. P. M., has been noted on page 363. On account of the magnitude of the effect, a series of ex-

periments was made in which the speed of the stirrer was the only variable. The results are shown in Fig. 8. An examination of the curves shows that, the other conditions being constant, the loss in weight by corrosion varies directly as the rate of stirring. The increase in the speed of corrosion with the increase in the rate of stirring is further illustrated by Fig. 9, in which the loss in weight of the plates for several different current densities is plotted against the number of revolutions of the stirrer per minute.

These results demonstrate that the rate of flow of acid solution over the metal surface is an important factor in determining both the amount of corrosion and the current density necessary to protect the metal. The decided increase in the speed of corrosion

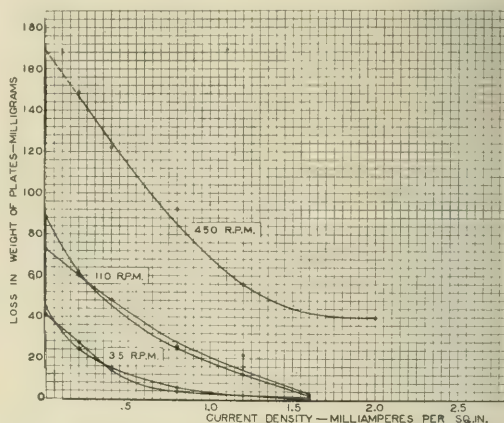


FIG. 8—EFFECT OF SPEED OF STIRRER ON RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY
Apparatus III. Duration of Test, 24 Hrs. $N/100 \text{ H}_2\text{SO}_4$

produced by circulation of the electrolyte is not surprising, since the flow of solution over the metal not only hinders the exhaustion of hydrogen ions in the vicinity of the anode, but provides a continual supply of oxygen and tends to destroy any film of hydrogen which may form on the surface of the cathode.

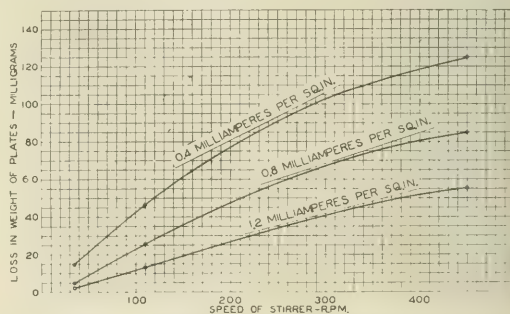


FIG. 9—EFFECT OF CURRENT DENSITY ON RELATION BETWEEN LOSS OF WEIGHT AND SPEED OF STIRRER
Apparatus III. Duration of Test, 24 Hrs. $N/1000 \text{ H}_2\text{SO}_4$

ACID CONCENTRATION.—That the rate of corrosion of iron or steel in sulfuric acid solutions increases with the acid concentration is well known. Though the acid concentration in the waters of nearly all streams

in which the corrosion of iron ordinarily occurs is much less than $N/100$ —the concentration used in most of the experiments described—the application of the method to more concentrated solutions seemed of sufficient interest to justify experiments with stronger solutions. Accordingly a series of experiments was made in which the concentration of sulfuric acid was varied from $N/1000$ to $N/10$. The results are represented by the curves in Fig. 10. They indicate that, although a considerably greater current density would be required, the method would be effectual even in $N/10$ H_2SO_4 . The curves for experiments with $N/100$

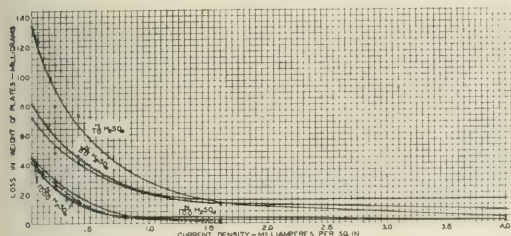


FIG. 10—EFFECT OF ACID CONCENTRATION UPON RELATION BETWEEN LOSS OF WEIGHT AND CURRENT DENSITY
Apparatus III. Duration of Test, 24 Hrs. Electrolyte Stirred, 35 R. P. M.

and $N/1000$ acid are practically identical, showing that between these limits of acid concentration there is no change in the rate or corrosion greater than the limit of error of observation. This result, though unexpected, was confirmed by repeated experiments.

especially in view of the variations found between the results of different experiments made under like conditions of acid concentration and rate of stirring, to be of value as a measure of the degree of protection against corrosion afforded by the current.

CURRENT DENSITY.—In the experiments which have been described, the following factors were found to influence the current density required to protect the corrosion of steel plates submerged in sulfuric acid solutions:

- Rate of stirring of electrolyte.
- Amount of oxygen present.
- Acid concentration.

Of these the last named is probably least important, especially in dilute solutions.

The rate of stirring of the electrolyte is by far the most important factor. Under normal conditions the supply of oxygen in the immediate vicinity of submerged metal surfaces depends largely on the rate of flow of solution over the metal surface. With the lowest rate of stirring used in the experiments, 35 R. P. M., and in acid concentrations not greater than $N/100$ a current density of from 0.5 to 0.8 milliampere reduced the corrosion loss to a negligible quantity, whereas with the stirrer rotating at a speed of 450 R. P. M. and a current density of 2.0 milliamperes the corrosion loss amounted to 25 per cent. of the loss on the unprotected plate.

HARKER'S EXPERIMENTS

From his experiments referred to above, Harker concluded that in employing the electrolytic process the cur-

TABLE I.—ELECTRODE POTENTIALS

Current density			POTENTIAL DIFFERENCE BETWEEN PROTECTED AND UNPROTECTED PLATE							
Current milliamperes	per sq. in.	Exp. 30	Exp. 31	Exp. 32	Exp. 35	Exp. 36	Exp. 37	Exp. 38	Exp. 39	Exp. 40
0.50	0.2	0.021	0.004	—0.021	—0.024	0.004	0.012	0.027	—0.005	—0.004
1.00	0.4		—0.003	—0.012	0.003	0.022	0.008	—0.018	—0.051	—0.024
2.00	0.8	0.198	0.025	0.102	0.078	0.073	0.044	0.012	0.000	0.015
4.00	1.6	0.433	0.114	0.237	0.186	0.187	0.108	0.102	0.081	0.090
10.0	4.0	0.723	0.289	0.429	0.372	0.392	0.304	0.315	0.295	0.303

Rate of stirring = 35 R. P. M.

Acid = $N/100$ H_2SO_4

POTENTIAL OF IRON ELECTRODES.—In the majority of the experiments, in addition to measuring the current flowing into the different electrodes, the potential of the individual electrodes was measured against a zinc electrode. Potential readings were made with a Siemens & Halske millivolt meter of 450 ohms resistance in series with a resistance of 17550 ohms. The results are given in Table I. The agreement between the potentials of electrodes having the same current density is only fair. In $N/100$ H_2SO_4 , and with a rate of stirring of 35 R. P. M., a current density of 0.8 milliamperes per square inch generally produced an increase in the potential of the iron electrode of about 0.04 volt. (In the table, potential differences are positive when the potential of the protected plate is positive to the unprotected plate, *i. e.*, when the potential difference between the zinc electrode and the protected plate is decreased by the protecting current.) As small an increase as 0.04 volt in the potential of the test plates sufficed, therefore, to protect them against corrosion. This effect is too small,

rent required to prevent corrosion might be calculated from the rate of corrosion of iron or steel under the given conditions and the electrochemical equivalent of iron. This conclusion he confirmed by one set of experiments in which, however, iron anodes were used. In experiments with a platinum anode, Harker found that the protection afforded by the current to the iron cathode was somewhat less than when an iron anode was used. He concluded that "the electrolytic process does not actually prevent metal from entering the solution from the cathode, for where the rate remains constant, deposition is taking place from the anode, yet the tendency of the metal to pass into solution is much diminished."

APPLICATION OF HARKER'S RULE.—In all of the experiments made by the present authors, a carbon anode was used. Harker's method of calculating the current density required to prevent corrosion was based on experiments with an iron anode. If, then, as Harker suggests, the protective action of the current is largely due to the transfer of iron from the anode

to the cathode it could not be expected that his method would hold for experiments with a carbon anode.

The method offers, however, such a simple procedure for arriving at the proper current density required to prevent corrosion that it seemed worth while to apply it to the results of the authors' experiments. In Table II are given the results of these experiments, to which have been added the values for the current densities calculated from the loss in weight of the unprotected plates and the electrochemical equivalent of iron. The "observed" values for the current densities in column 6 were obtained graphically from the curves in Figs. 2, 3, 4, 7, 8 and 10. The agreement between the observed and calculated values is remarkably good. The differences are well within the experimental error.

It may, therefore, be concluded that Harker's method of calculating the current density required to prevent corrosion, from the loss in weight of the metal under the given conditions, is not limited to cases in which an anode of the same metal is used.

TABLE II

Results plotted in figure	Number of Exp.	Acid conc.	Stirrer R. P. M.	Length of run, Hours	Current density milliamp. per sq. inch		Weight lost by un- protected plate (mg.)
					Obs.	Calc.	
					Apparatus I:		
2....	4	N/5	...	45.0	3.0	2.2	344.6
3....	6	N/10	...	47.0	3.0	3.4	551.5
3....	7	N/10	...	20.0	3.0	2.0	140.5
3....	9	N/10	...	23.5	1.5	2.7	221.0
3....	8	N/10	...	22.0	1.5	2.0	151.5
Apparatus II:							
4....	11	N/10	...	22.5	0.45	0.5	43.0
4....	12	N/10	...	22.0	0.45	1.2	93.5
7....	39	N/100	35	24.0	1.6	1.3	75.9
Apparatus III:							
7....	38	N/100(a)	35	24.0	1.6	1.0	64.3
7....	40	N/100	35	24.0	0.8	0.7	44.6
7....	30	N/100	35	24.0	0.8	0.7	41.4
8....	48	N/1000	450	24.0	2.0	2.7	170.0
8....	45	N/1000	110	24.0	1.6	1.4	88.3
8....	46	N/1000	110	24.0	1.6	1.2	72.8
8....	42	N/1000	35	24.0	0.8	0.7	44.5
8....	41	N/1000	35	24.0	0.8	0.6	41.0
10....	51	N/10	35	24.0	1.6	2.2	133.8
10....	49	N/50	35	24.0	1.2	1.1	71.3
10....	50	N/50	35	24.0	1.2	1.3	80.9

(a) O₂ Oxygen saturated.

(a) Oxygen saturated.

THE NATURE OF THE ACTION OF THE ELECTRIC CURRENT

Harker's view that the current does not actually prevent metal from entering the solution from the cathode, and that its protective action is due to the deposition of metal from the anode, is contradicted by the authors' experiments in which carbon anodes only were used. The action of the current, then, is to prevent the formation of ferrous ions at the cathode by increasing its negative charge. In the absence of any depolarizer, especially of dissolved oxygen, an infinitesimal current should produce an electromotive force large enough to neutralize the solution tension of the metal. When oxygen is present, it combines with the hydrogen ions liberated at the cathode and hinders polarization. The supply of hydrogen ions furnished by the current must be equivalent to the

supply of oxygen in the vicinity of the cathode before the solution tension of the cathode can be completely neutralized.

CONCLUSION

It has been shown that the corrosion of iron submerged in sulfuric acid solutions may be prevented by imposing a counter E. M. F. The density of the current required to prevent corrosion depends on various factors, the more important being acid concentration, amount of dissolved oxygen and degree of circulation of electrolyte. The influence of these factors has been studied and curves have been given showing the current density necessary under various conditions. It has been found that the current density required can be calculated, within the limit of experimental error, from the loss in weight of the unprotected metal under the given conditions.

U. S. BUREAU OF MINES
PITTSBURGH, PA.

PAINT AS AN ENGINEERING MATERIAL¹

By MAXIMILIAN TOCH

The progress that paint chemistry has made since 1905 is by far greater than the progress that was made from its earliest invention up to that date. It is very difficult for me to imagine that my first book on "The Chemistry of Paints" stimulated others to continue the work which I had started, and if the little that I have done to enlighten the manufacturers and consumers has brought about the progressive results, I certainly have been rewarded for all the work I have ever done on the subject.

The first skyscraper ever built was the Gillender Building, corner of Wall and Nassau Streets, which was razed two years ago. Chemists knew before this building was demolished that linseed oil paint was not the best material for the protection of steel of large buildings. The question as to whether our monumental buildings are permanent has been a source of great worry to many chemists and engineers. Fortunately, if any of the steel contained in buildings like the Woolworth Building, Metropolitan Tower, the Singer Tower and dozens of others should show signs of corrosion and disintegration, the process is so slow that preventive methods could be applied, for a beam could not corrode in a masonry wall without cracking or bulging the wall. I have in mind one building in Maiden Lane where this actually occurred; the wall of the fifteenth floor was cut away, the corroded beam exposed, thoroughly scraped, painted and reinforced, surrounded by concrete, and the brick wall replaced.

From the street level up, every skyscraper in the world is safe, but from the street level to the grillage beams is the dangerous point. Of course, a small building could be "jacked up" and a grillage beam replaced. In large buildings—two of which I have in mind—where the grillages were affected by leaky electrical currents, the foundation beams were uncovered, scraped clean and painted, and then a grout

¹ Abstracted by the author from an address presented before the N. Y. Section of the American Chemical Society, Chemists' Club, Feb. 7, 1913.

of almost pure neat cement injected all over the surface. Of course, it would be out of the question to "jack up" a building like the Woolworth Building, or the Metropolitan Life, even though Archimides said, "Give me a fulcrum and I will move the world;" but it is a source of great satisfaction to know that

bridges would last ten years if they were not repeatedly painted and watched. The railroads are much wider awake to this condition than the municipal governments. Politics and paint do not mix very well, as is evidenced by the condition of some of our bridges. It may be very safely said, that all of our elevated



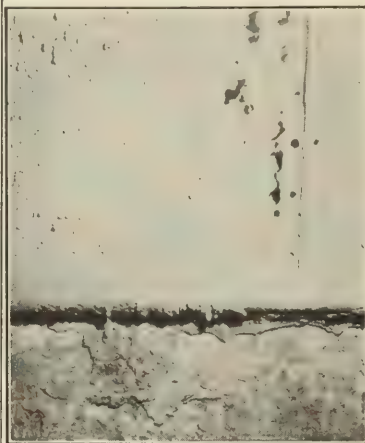
STEAM PUMP OF MAINE

Submerged 13 years. Put in excellent condition by a few repairs



MAST OF MAINE

Had 15 coats of paint. Exposed to elements for about 11 years and still in good condition



INTERIOR PLATES ALONGSIDE COAL HOIST

Complete corrosion in spots only

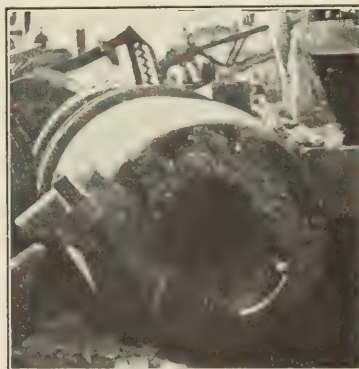
engineers and architects in charge of these buildings have taken sufficient precautions to prevent any danger whatever, either from electrolysis by means of stray currents, or from corrosion by means of dampness. All the sensational talk about the danger of the newer skyscrapers not lasting fifty years is utter "rot," for not one of these buildings is so con-

railroads in New York City and all of the battleships of the United States Government depend for their life on the frequency with which they are painted. My examination of the battleship "Maine" when the wreck was uncovered last year showed that not a vestige of paint remained, and it furthermore showed that wherever steel and copper, or iron and bronze,



BRONZE BINNACLE AND STEEL VENTILATOR SHAFT OF MAINE

Electrolytic corrosion: bronze preserved and steel dissolved



ELECTROLYTIC CORROSION BETWEEN BREECH LOCK AND STEEL OF 10-IN. GUN

structed that should any danger result it could not be remedied in due time.

That paint is an engineering material of incalculable value is evidenced by the fact that none of our

were in close proximity, an electric battery was formed, and the iron was completely dissolved.

The aphorism that "Cement protects steel permanently against corrosion" needs some little explanation. Unfortunately, this saying is true and correct,

and still more unfortunately, there is no such thing in building construction as cement. I know that this sounds ridiculous in view of the fact that in 1912 upwards of sixty million barrels of cement were used in concrete construction, and a large part of it was used in reinforced concrete construction, which means that steel rods were embedded in it; but you must bear in mind that cement is never used as such in any kind of construction, but a mixture of cement, sand



CONCRETE WALL SHOWING RUST OF REINFORCING ROD

and broken stone is used; the average percentage of cement contained in most engineering operations is 15 per cent., so that when we talk about cement being used we really mean concrete, which under many circumstances is a nondescript mixture. It is a trifle out of place for me to go into the reasons why cement is not used, but why concrete is used, and only one or two examples will suffice to indicate. Cement is entirely too rich and entirely too expensive to use by itself, and sand and other ingredients which are added to cement can never under any circumstances be classed as adulterants, particularly sand, because when a cement grout is used that is too rich it will crack or craze, as the case may be. If you were to drive a tack with a 10 lb. sledge hammer you would undoubtedly accomplish the object and you might possibly destroy or break the material into which the tack was driven, but if you use a weak little 2 oz. hammer you accomplish the result better and without any ill effects. The same comparison holds true as to the use of aggregate in cement. The dilution of the cement with inert material saves money and gives better engineering results, but yet when we add 85 per cent. of material which may be cinders, broken stone, or sandy material containing more or less soluble salts, and when the workmanship is taken into consideration, and voids are produced, it is quite obvious that rust may start in concrete surroundings, and the small percentage of cement will be insufficient to overcome or check the oxidation. There is a wall in the City of New York which shows this fact very markedly, and in a wall of this type an insulating paint or insulating material would have prevented the oxida-

tion of the steel and the subsequent cracking of the wall.

This then leads me to the general subject of the more modern type of paint containing no saponifiable oil, but made entirely of such materials as are unaffected by alkali. Such tremendous structures as the Pennsylvania Terminal in New York City, and Metropolitan Life Tower and Building, the Woolworth Building, and the newest and largest of all engineering structures, the New York & Connecting Railway—not yet finished—are types of modern structures in which the old-time linseed oil paints have been superseded, and protected by more scientific paints. Perhaps the most remarkable fact in all these instances is that fifteen years ago perhaps, one concern in the United States started a campaign of education and convinced many prominent and well-known engineers that paint was an engineering material and that no one material is suitable for all purposes with the result that the paint industry has been raised from empiricism to an exact science. Ten years ago nobody dreamed of painting cement floors or cement walls on account of the tradition that it was impossible to paint concrete. It is quite true that it is impossible to paint new concrete with a linseed oil paint owing to the resulting chemical reaction of the combination of the oil and the lime in the concrete, and yet when the first patent was taken out on this subject nobody infringed because it was believed that it could not be a success, and after it was demonstrated that this was a success it was the same story as "Columbus and the egg," and everybody imitated and made a business of it.



WOOLWORTH BUILDING FOUNDATION GIRDER PAINTED WITH AN INSULATING PAINT

The United States Navy, through one of its most efficient Naval Constructors, Mr. Henry Williams, has kept pace with the paint progress, and Mr. Williams' article, a treatise on the subject of "Newer Paint Conditions in the United States Navy," read

before the Eighth International Congress of Applied Chemistry, was copied not only by every paper in the United States but was heralded throughout Europe; and those who want to know what excellent progress has been made in this branch of the Government, I

been the subject of considerable investigation, for it is self-evident that the quality of the set of a cement determines the ultimate strength of the concrete of which it is a constituent.

Experimenters do not seem to agree very well as to the mechanism of this setting, nor as to the factors that exert the greatest influence during the time that the hydrolysis is taking place. Consequently there is a diversity of opinion as to the method to employ during the processes of manufacture or as to what subsequent treatment the cement must undergo, in order that the manufacturer may at all times put upon the market a cement whose behavior may be predicted, and whose quality will show no deterioration during long-time storage.

The consensus of opinion seems to be that the initial set of a cement is due to some action for which the aluminates are responsible, or to which they at least contribute in a large measure.

Also it seems to be quite well agreed that the retarding action of gypsum is due, if not to the formation of a double salt with the aluminates, at least to the fact that it slows down their hydrolysis and consequently delays the initial set of the cement.

It has been the writer's good fortune to have been at various times connected with the operation of Portland cement plants using materials abnormally high in alumina, and he invariably found that it was impossible, under those conditions, to vary the lime content of the cement over any extended range without causing trouble. If the lime was carried high (63-64 per cent.), the cement approached too closely the danger line of unsoundness, while if it dropped too low (60.5-61), the factory was troubled with quick setting cement.

Quick setting cement resulting from such operation is not so responsive to the retarding action of gypsum as one more nearly normal in composition. Sometimes it will be quick setting direct from the grinding mills, while at others it will develop a quick set after short storage. Quite often it will show a reversion to quick set if an excess of gypsum is added. The writer had his attention called to a condition where two sections of a plant were operated with differences of 30 per cent. in the gypsum added.

None of the cases of quick set in the writer's operating experience ever developed serious difficulties, as the setting times were watched very closely, and at a suspicion of trouble in the stored materials a quick



TELESCOPIC PHOTOGRAPH OF THE 12TH STORY OF THE GILLINDER BUILDING, SHOWING THE STEEL IN PERFECT CONDITION, BUT NO PAINT LEFT. EACH BOLT-HEAD IS EXCELLENTLY PRESERVED

would refer to his excellent treatise on the subject which is to be found in the transactions of the Eighth International Congress of Applied Chemistry.

320 FIFTH AVE., NEW YORK

CONTROL OF INITIAL SETTING TIME OF PORTLAND CEMENT¹

By E. E. WARE²

It is well known that Portland cement, as burned in the rotary kiln, is so quick setting that it cannot be used without the addition of some retarding material, such as gypsum or plaster of Paris. It is not necessary to make this addition of retarding agent when dealing with the product of a set kiln, probably for the reason that the cement contains the ash of the fuel as well as most of the sulfur.

Occasionally there has been reported a cement of such a nature as to be quick setting even after the addition of the regular amount of retarder, and this paper is in the nature of a report on the commercial manipulation of a 100,000 barrel lot of such quick setting clinker. The manufacturer was interested, *first*, in correcting the material on hand, and *second* in establishing a routine of operation that would prevent a recurrence of the trouble.

The setting and hardening of hydraulic mortars has

¹ Paper presented at Fifth Annual Meeting of the American Institute of Chemical Engineers, Detroit, December, 1912.

² Credit is due to L. C. Nodell and P. H. Chang for the experimental work in connection with this paper.

cement was mixed out with a slower one, preferably one having a tendency toward unsoundness, the combination seeming to remain perfectly stable and not to require any further additions of gypsum. Also at any indication of quick set in the material coming from the mills, the lime in the mix was immediately raised, a procedure that never failed to correct the trouble.

This seems to agree with the experience of Meade,¹ who states that quick setting cements that have come under his observation are low lime cements. He states also, that he has retarded the set of plastered cements that have gone quick, by addition of calcium hydrate or even calcium oxide.

It seems to be, however, a direct contradiction to the statements of Reibling and Reyes,² who state that all quick setting cements contain free lime, remain quick setting so long as the lime is in the form of oxide, become slow setting as the lime hydrates, again quicken when the hydrate changes to carbonate, and finally become slow setting as the hydraulic constituents become inert through long exposure.

In view of these interesting experiences with quick setting cement, it was with considerable interest that the writer responded to an invitation from a cement company who reported a large stock of clinker as quick setting and beyond the influence of the ordinary corrective methods. The clinker was the regular fall run, stored over winter, the plant being one that operated on marl, and followed the usual practice of burning a large stock of clinker during the late fall months to supplement their stock for the early spring demand, which opens before the ice leaves the lakes from which they dredge their supply of

the rest of the fall grind showed a normal setting time.

Experiments were run to try the effects of different added materials, such as plaster (instead of gypsum), hydrated lime, calcium chloride, and acids; but none of them seemed to be successful in retarding the set.

At the same time other experiments were tried along the line of hydration, as recommended by Bamber.³ These were highly satisfactory, the cement ground from clinker, which showed a set of 3-5 minutes under ordinary procedure, being slowed to $2\frac{1}{2}$ -3 hrs. when hydrated to the extent of less than two per cent.

It seemed to make little difference how this water was added, as is illustrated by the following experiments:

1. The cement, after grinding with the usual amount of gypsum, was heated in a closed tube, the idea being that the water resulting from the dehydration of the gypsum might prove sufficient for the hydration of the troublesome constituents. This proved to be the case.

2. The clinker was heated to approximately 100 C. and ground while hot, the result being the same.

3. The ground cement was dropped through a vertical tube through which a small cloud of steam was rising; subjection to this atmosphere for even so short a time as that necessary for it to drop through a tube thirty inches long was entirely sufficient to retard the set.

4. Water to the extent of three per cent was added to the ground cement, mixed rapidly by hand, and then placed in a laboratory pebble mill where it was mixed mechanically for a short time. The set was delayed, but not so uniformly as by the other methods.

5. Water was sprinkled on the cold clinker as it was fed to the grinding mills at the factory. This treatment was satisfactory so long as the water supply could be kept constant; but the mill operators could not be depended upon to regulate the supply properly, and the idea was abandoned as impracticable.

6. Steam was turned into the conveyor leading from the mills. The results from this method were not dependable, and the scheme was dropped as being too uncertain to be safe to use.

The method that was finally adopted was that of heating the clinker and grinding while hot. This method proved entirely satisfactory for the treatment of the greater part of the quick clinker, the remaining being left over until the kilns should be in operation, when the old clinker was ground with the new, the new being purposely not thoroughly cooled.

The adoption of this method was largely influenced by the layout of the plant which, with the clinker pile lying alongside of the kilns and for their full length, made it a simple matter to send part of the clinker through one kiln, and mix it on its return with a quantity of cold clinker. The gypsum used was thoroughly wetted and added to the clinker just before it reached the mill hoppers, these hoppers be-

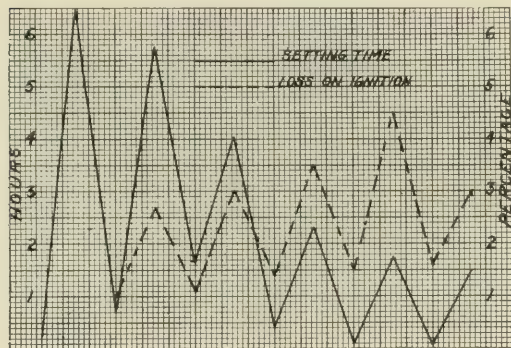


FIG. 1.

marl. An interesting circumstance in connection with the problem was that although some cement ground in the late fall showed quick setting, the majority of it was perfectly normal except that it would not stand any large additions of quick setting material without itself showing an earlier set. Inquiry developed the fact that this quick setting cement was ground during a short period that the kilns were out of operation, and that when the kilns were started

¹ "Portland Cement," Meade, p. 416.

² *Philippine Journal of Science*, 1911, 207.

³ *Concrete and Const. Eng.*, 1909, (4) 196.

ing kept only partially filled in order that the clinker might not have time to cool or to dehydrate the gypsum before reaching the mills.

From a consideration of the plant, it was a simple matter to explain the quick setting cement that was ground in the fall. As the stock of clinker grew larger, there was left only one place to discharge the kiln output, and that was at the part of the clinker pile farthest away from the kiln discharge, a point which is nearest to the mills. This meant that for at least the last few weeks the mills were grinding hot clinker; but for the few days that the mills were operated while the kilns were off fire they would be supplied with cold clinker, and so ground out a small amount of quick setting cement.

The table of analyses shows four analyses of quick setting cements, 1-4, and three slow setting cements, 5-7, from the factory stock. The set 8-12 belongs to a series of laboratory cements made from the same raw material, in an endeavor to establish the safe limits for factory operation.

TABLE I—ANALYSES OF CLINKERS (PERCENTAGES)

NUMBER	1	2	3	4	5	6	7	8	9	10	11	12
Loss	1.0	0.7	2.4	3.0	1.3	0.4	0.03	2.4	1.16
Silica	21.4	22.0	22.4	22.7	22.25	21.9	22.48	24.9	24.4	23.7	23.7	23.9
Ferric oxide	5.1	3.9	3.6	4.0	4.4	4.8	4.2
Alumina	6.4	7.0	7.4	6.6	6.35	7.3	7.3	11.7	10.9	10.4	10.1	9.8
Lime	61.0	61.3	61.6	59.8	62.5	61.7	62.9	59.4	58.5	61.4	63.3	61.7
Magnesia	2.3	2.4	2.1	2.3	2.0	2.0	2.2	2.11	2.17	2.14
SO ₃	1.74	1.57	0.74	1.83	1.57	1.54	1.58	2.21	1.58	1.57	1.36	1.34
SiO ₂ /R ₂ O ₃	1.85	2.02	2.05	2.13	2.07	1.8	1.95	2.13	2.23	2.28	2.36	2.46
Set	quick	quick	quick	quick	normal	normal	normal	quick	quick	quick	3 hrs.	3.5 hrs.

These experimental burns were carried out in a small experimental kiln designed by Prof. E. D. Campbell,¹ and used by him in all his work on the composition of Portland cement and the influences that affect its constitution and characteristics.

The clinker from these burns was carefully sorted and all material that showed any signs of under-burning was discarded. The good clinker was then crushed and ground with gypsum.

This set of analyses shows alumina in a fairly high percentage, but fails to show why this alumina has such a decidedly quickening effect under conditions not entirely accounted for by the composition of the cement. In an endeavor to locate some of the influencing factors, a few further experiments were carried out.

Quenched clinker from these high alumina samples showed quick setting if perfectly dried, but slow setting if only air-dried. Steamed clinker when air-dried showed a retarding set when ground with plaster.

All cements that have come under observation develop quick set when heated to 350-400° C. This includes a number of commercial samples of varying composition and compounded from widely different materials. Two commercial cements that had been stored since 1899 and which were presumably in their last stage of slow set, had their initial setting time decreased from 3 1/2 hours to 1 minute. There was a loss in weight during heating of only 0.15 per cent.

A cement with a setting time of fifteen minutes was treated alternately with water and heat and showed a setting time curve as in Fig. I. At each stage in this addition of water and subsequent heating to 350-400° C., a sample of the material was strongly ignited and showed losses corresponding to the dotted curve on Fig. I.

From a consideration of the curve it would seem as though the water must have been present in two different conditions, for although the cement showed a continuously increasing amount of water, the set was not correspondingly slowed. This may be partially due to the fact that the heated cement retained some water in such a condition that it was not driven off when heated to 350° C., in which condition the water did not seem to exert much influence on the setting time.

In an effort to establish whether it was the gypsum or the cement that was affected by heat, a cement containing no gypsum was heated and afterward mixed with the normal amount. It showed a slow

set. Another example of the same material, unheated, was mixed with gypsum that had been heated. While it required a larger amount (5 per cent)² to retard the set, it showed a normal setting time.

Any one of these slow setting samples would develop a quick set upon heating. In the case of the cement carrying five per cent dead burned gypsum, it required a much longer time of heating than in the case of those samples carrying the smaller amounts. The times of heating varied from six hours to forty-eight hours in the different samples. Dry slaked lime showed no appreciable loss of water under the same conditions of heating.

The whole set of quick setting cements was tested for free lime according to the microscopic method described by Prof. A. H. White.³ There seemed to be no indications of free lime.

Although it may be impossible to draw any definite conclusions from this rather incomplete line of experiments, it seems to be certain that in this instance, at least, the quick setting was not due to free lime.

This experimental work is to be continued, in the hope of gathering further data that may assist in clearing away the uncertainties in regard to the role that alumina and gypsum play during the initial setting of Portland cement.

UNIVERSITY OF MICHIGAN
ANN ARBOR

¹ Meade and Gano, *Chem. Eng.*, 1, 92.

² THIS JOURNAL, 1909, (1) 5.

³ *J. Am. Chem. Soc.*, 24, 248.

TESTS TO DETERMINE THE COMMERCIAL VALUE OF WOOD PRESERVATIVES. A PROGRESS REPORT¹

By HOWARD F. WHEISS

ACKNOWLEDGMENTS

The author wishes to acknowledge the services rendered by the following members of the Forest Products Laboratory who performed the experiments herein described: F. M. Bond, in charge of Wood Preservation; L. F. Hawley, in charge of Chemistry and Distillation; C. H. Teesdale, Engineer in Forest Products; Ernest Bateman, Chemist in Forest Products; C. J. Humphrey, Pathologist, Bureau of Plant Industry.

Acknowledgment is also made to Ira H. Woolson, Consulting Engineer, the National Board of Fire Underwriters, for his very courteous and valuable assistance in the inflammability tests.

INTRODUCTION

A list of the various substances that have been used or suggested for preserving timber from decay would embrace many of those known to industrial chemistry. By-products for which no use could be found have generally taken their last stand as possible preservatives of wood. We have had sent to us for tests the condensed fumes of smelters, the waste liquors of pulp plants, the refuse of tanneries, the skimmed milk of creameries, and miscellaneous assortments of compounds under trade names. Many of these have been culled without any test whatever because the claims made for them were manifestly impracticable. Those, however, which appeared meritorious, or about which numerous inquiries from various consumers were received, were admitted to test.

The object of the tests here described is primarily to obtain information on the practical value as wood preservatives of those compounds or chemicals which fall within this latter classification, so that intelligent replies might be given to the various inquiries received. Further, it was thought that such an investigation would show clearly the deficiencies of present practice and pave the way for increasing its efficiency by suggesting lines for original research.

From 40 to 90 per cent., or an average of about 70 per cent., of the total cost of treating wood is in general due to the preservative alone. The most promising field for decreasing the cost, therefore, lies in decreasing the cost of the preservative used. In ordinary treatments with coal-tar creosote it is common practice to inject approximately ten pounds of the oil per cubic foot of wood, although about one-fifth of a pound will prevent fungous growth; in other words, a factor of safety of about fifty applied to the entire volume of wood is used. The safe reduction of this factor offers one of the many interesting problems.

Before undertaking investigations with new compounds, or improved methods of handling the old ones, it was thought best to first collect certain pertinent data which would be of most immediate value and which would broaden the investigator's viewpoint. The tests here described comprise what has

been accomplished thus far and should, therefore, be considered simply as preliminary to the more serious problems involved.

PROPERTIES INVESTIGATED

The practical value of a preservative depends very largely upon the conditions under which it is used, and, as these vary considerably, the investigations must necessarily be broad. With this in view, and with a study of the inquiries received as a basis, the following points were studied in these tests:

1. The important chemical and physical properties of the preservative.
2. The effect of the preservative on the strength of the wood treated with it.
3. The ability of the preservative to penetrate and diffuse through wood.
4. The permanency of the preservative after its injection into wood. This involves a study into its volatility and leachability.
5. The combustibility of the wood treated with the preservative.
6. The toxic efficiency of the preservative in inhibiting the growth of wood-destroying fungi.
7. The corrosive action of the preservative on steel.
8. The effect of the preservative on paint applied to the wood subsequent to treatment.

TABLE I

PIECE NO	SIZE	LATER CUT INTO	
		PIECE NO (MARK)	SIZE
1	1 1/2 x 1 1/2 x 13	1-1 1-2	1 1/2 x 1 1/2 x 9"
2	"	2-1 2-2	"
3	"	3-1 3-2	"
4	"	4-1 4-2	"
5	"	5-1 5-2	"
6	"	6-1 6-2	"
7	1 1/2 x 2 x 13		
8	"		
9	"		
10	"		
11	1 1/2 x 1 1/2 x 13	11-1 11-2 11-3	1 1/2 x 1 1/2 x 6"
12	"	12-1 12-2 12-3	"
13	"	13-1 13-2 13-3	"
14	"	14-1 14-2	1 1/2 x 1 1/2 x 6 1/2"

RECUT INTO	
PIECE NO (MARK)	SIZE
14-1-1	1 1/2 x 1 1/2 x 2"
14-1-2	"
14-1-3	"
14-2-1	"
14-2-2	"
14-2-3	"



FIGURE I

Since the investigations were started two other groups of inquiries have become apparent; namely, the effect of the preservative as an electrolyte and in contaminating drinking water. No systematic tests on either have, however, been made, nor any tests which pertain to a special or limited use.

METHODS OF TEST

The methods by which the various tests were conducted will be only briefly described.

Thoroughly air-seasoned eastern hemlock (*Tsuga canadensis* L.) was selected as the wood best suited

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

for the tests because of its low inherent resistance to attack, by fungi, its comparative uniformity of treatment, and its accessibility. Only perfectly clear, straight-grained, and uniform material, free from all mechanical and physical defects, was used—this being cut into test pieces $12'' \times 13'' \times 1\frac{1}{4}''$ and recut as shown in Fig. 1 and Table I.

Chemical and Physical Properties of the Preservatives.—Under this heading were tested, by standard methods, the chemical composition of the preservative, its specific gravity, viscosity, odor, flash, and burning points. In all distillations the apparatus described in *Forest Service Circular 112* was used.

The specific gravity was determined chiefly by a hydrometer or by a Westphal balance. Viscosities were obtained by using the Engler orifice viscosimeter at various temperatures. The flash and burning points were tested by heating the preservative at a rate of 2°C. per minute in an open flash-point tester, passing a small flame over the surface every minute.

Injection of the Preservative.—Pieces Nos. 4, 5, 6, 7, 11, 12, 13, and 14-2 were injected with the preservative. Before injection they were oven-dried at 100°C. , when they were weighed, and impregnated in the cylinder shown in Figure 2. The simplest procedure (Bethell process) was followed. For example: After the wood was placed in the cylinder the preservative was admitted, displacing the air, until the cylinder was completely filled; a hydrostatic pressure of about 50 pounds per square inch was then applied until the desired absorption was obtained, when the specimens were removed and weighed within 24 hours; when necessary higher pressures were used.

Strength Tests.—Pieces 1, 2, 3, 4, 5, and 6, the latter three treated with the preservative, were tested in bending to failure in an ordinary 30,000-pound testing machine, using a center load over a 12-inch span. Care was taken to have all specimens at approximately the same moisture content at the time of test (about 6 per cent).

Penetration of the Preservative into Wood.—Sticks 4, 5, and 6, after the strength data had been obtained on them, were split and the depth and character of the penetration recorded. This could usually be done visually, but with those preservatives which in aqueous solution were colorless, an aniline dye was used or the specimens were chemically analyzed.¹

The results from these tests were used to supplement those secured from pieces 8, 9, and 10, which were tested in a specially constructed penetration apparatus (see Fig. 3) operated as follows: A hole, one inch in diameter, was bored in the center of each stick, *E*, to a depth of three-fourths inch. The stick was then raised to a temperature of about 180°F. and clamped between two iron discs, *F* and *F'*, so that the preservative could be forced into the hole under a constant pressure and temperature. For oils, the length of the pressure period was 30 minutes, and for water-soluble salts, 3 minutes, with the exception of sodium silicate, for which the time was

¹ It was found by repeated tests that water and the dye had a tendency to penetrate in some cases slightly farther than the preservative, although the difference was of no practical significance.

prolonged to 30 minutes. The time it took to penetrate the wood longitudinally was noted, after which the specimen was sawed longitudinally and transversely through the center lines and the penetration radially, tangentially, and longitudinally was studied.

Volatilization Tests.—The volatility tests were made on oils only. Within three hours after stick 12 had been impregnated it was recut into three pieces, each $1\frac{1}{4}'' \times 1\frac{1}{4}'' \times 4''$ in size, weighed separately, and placed in the volatility apparatus (see Fig. 4) which consists of an air-tight, metal box, $15'' \times 24'' \times 30''$, through which was passed a constant current of air

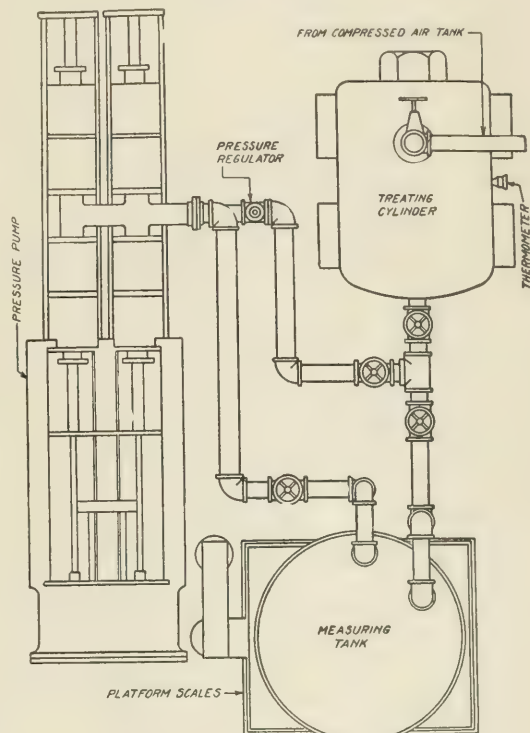


FIG. 2—IMPREGNATION APPARATUS

previously dehydrated by passing through sulfuric acid. The box was heated to 30°C. by electric lamps, the temperature being automatically controlled within 1°C. The treated specimens were removed and weighed at weekly periods for three months. The loss in weight was taken as representing the amount of the preservative volatilized.

Leaching Tests.—Leaching tests were made on the water-soluble salts only. Within three hours after stick 13 had been impregnated it was recut into three pieces, each $1\frac{1}{4}'' \times 1\frac{1}{4}'' \times 4''$ in size, and weighed separately. Generally, within 48 hours of impregnation these pieces were submerged in a glass jar containing 300 cc. of distilled water at room temperature; this water was changed at stated intervals and analyzed for the presence of preservative. The total time of leaching was four weeks. To check the amount of the preservative remaining in the wood after the total

submersion, the specimens were shredded and chemically analyzed.

Inflammability Test.—The crib and shavings tests ordinarily used in examining the combustibility of wood were all discarded because of inability to get sufficiently concordant results. This made it necessary to develop original apparatus (see Fig. 5) which consisted of a silica tube, wrapped with nichrome ribbon. An iron tube fitted with a mica sight was cemented below the silica tube.

The specimen of wood, after being lowered in the silica tube, was heated at a uniform rate, by passing twenty-four amperes of electric current through the nichrome ribbon. Temperature readings were obtained from a thermocouple placed beside the specimen

specimens were first air-dried and then oven-dried before ignition. When the preservative was an oil, one inflammability test was made within twenty-four hours after impregnation and another after three months' seasoning in the volatility apparatus.

Toxicity Tests.—Because of the importance of toxicity tests and the inherent objections to various established methods of testing, three methods were followed:

1. Petri-dish method, in which the culture medium was made of juice from one pound of beef, 25 grams Löflund's malt extract, 20 grams agar-agar, and 1000 cc. of distilled water.

2. The injection of the preservative into wood with a subsequent exposure to an isolated fungus (*Fomes annosus* Fr.) in sterilized jars.

3. The injection of the preservative into wood with subsequent exposure to various fungi in a fungus pit. Only those fungi which were known to attack wood substance were used.

At present, degrees of decay are determined visually. This method permits of too great error due to the personal equation. To overcome this the extent of attack in these tests was determined by noting the loss in weight of the wood after infection and by forcing a steel ball into it before and after decay, recording the force required to sink the ball to its semi-diameter.

Corrosion Tests.—To determine the corrosive action of the preservative on steel a strip of flange steel of the quality specified by the American Society for Testing Materials, August 16, 1909, was submerged in the preservative and heated to a constant temperature of about 98° C. The preservative was changed every week for four weeks in the case of oils; with aqueous solutions it was changed every day for one week. The difference in the weight of the steel before and after submersion was taken to indicate its corrosion. All depositions on the surface of the metal were removed as nearly as possible with a rubber policeman each time the preservative was changed. At the end of the test, where electrolytic deposition of metal had taken place, the deposited metal was removed by acid and its amount determined by an analysis of the acid solution. The deposited metal thus obtained was added to the loss of iron and this total represented the total corrosion.

Paint Tests.—The treated wood was first air-seasoned for about one month and then coated with white paint (30 pounds of lead oxide to one gallon of linseed oil), noting the color change which subsequently took place.

RESULTS

In the following brief summary of results already secured the author wishes to strongly emphasize that they are tentative only and may be changed in view of subsequent tests, as the field covered is new and errors in manipulation, not at present apparent, might exist. Every feasible precaution, however, was taken to avoid errors and when these were uncontrollable they are so mentioned.

Effect of the Preservative on the Strength of Wood (for details see Table III).—As a greater accuracy

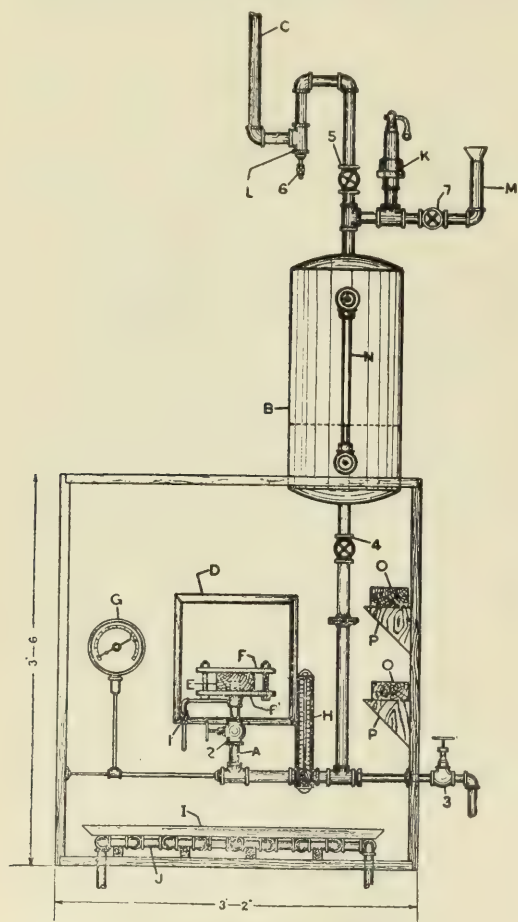


FIG. 3.—PENETRANCE APPARATUS

and reading direct from a Hoskins pyrometer. A pilot light was used to ignite the gases distilled from the wood. Compressed air partially dehydrated by expansion was passed through the apparatus, its intensity being indicated by a sensitive liquid manometer. Three untreated test specimens were burned as a check against the three treated specimens. When the preservative was a water-soluble salt, the test

TABLE II—CHEMICAL AND PHYSICAL PROPERTIES OF THE PRESERVATIVES

Preservative designated by co-operator as	Specific gravity	Degrees C.	Flash point ° C.	Burning point ° C.	Viscosity (Temperature ° C.)				ODOR	REMARKS
					10	50	30	95		
Coal-tar creosote.....	1.048	60	93	100	3.1	1.7	1.4	1.1	Strong creosote	Graded as "C"
Coal-tar creosote, Frac. 1....	0.934	60	62	69	...	1.1	1.0	0.95	Like toluene	Includes oils distilling between 0-205° C.
Coal-tar creosote, Frac. 2....	1.003	60	79	85	1.0	Strong like naphthalene	Includes oils distilling between 205-250° C. Solid at room temperature
Coal-tar creosote, Frac. 3....	1.045	60	103	110	2.45	1.4	1.2	1.1	Strong coal-tar creosote	Includes oils distilling between 250-295° C.
Coal-tar creosote, Frac. 4....	1.088	60	130	136	1.51	1.11	Mild coal-tar creosote	Includes oils distilling between 295-320° C. Would not flow at 30° C.
Coal-tar creosote, Frac. 5....	1.150	60	172	178	80.0	2.6	Mild coal-tar creosote	Includes residue above 320° C.
S. P. F. carbolineum.....	1.127	16	133	157	...	4.4	2.3	1.25	Tarry (mild)	These compounds are similar in many respects. Their exact composition was not determined
Avenarius carbolineum.....	1.126	16.5	139	166	...	7.5	2.4	1.25	Tarry	
C. A. Wood preserver	
Hardwood tar	1.195	60	90	*	...	17.5**	6.3**	1.4**	Disagreeable pyroligneous	* Water boiled off preventing burning ** Viscosity orifice viscosimeter
Wood creosote (Douglas fir)	1.052	60	45	85	...	15.2	4.9	1.4	Disagreeable pyroligneous	This resembled a tar more than a "creosote"
1.07 oil.....	1.058	60	48	65	16.0	3.7	2.0	1.2	Like kerosene	A water-gas-tar product
Timber-asphalt.....	1.063	60	240	260	99.2	5.2	Like crude oil	A residuum of petroleum
Copperized oil.....	0.937	25	125	164	...	18.0	5.1	1.5	Like crude oil (mild)	Contains 0.34% copper
Fuel oil.....	0.87	60	72	101	2.8	1.57	1.3	1.1	Like crude oil (strong)	A crude petroleum
Zinc chloride.....	1.028	20	Same as water				Odorless	Contained 2.67% ZnCl ₂
Zinc sulfate.....	1.033	20	Same as water				Odorless	Contained 5.9% ZnSO ₄ ·7H ₂ O
Zinc sulfate (by-product)....	1.040	20	Same as water				Odorless	Contained 6.8% ZnSO ₄ ·7H ₂ O
Sapwood antiseptic.....	1.027	20	Same as water				Odorless	Contained 2.92% NaCl Contained 0.246% CaSO ₄
B. M. preservative.....	1.025	20	Same as water				Odorless	Contained 0.246% ZnSO ₄ ·7H ₂ O Contained 0.182% CuSO ₄ ·5H ₂ O
Sodium silicate.....	1.074	20	Same as water				Odorless	Contained 0.06% FeSO ₄ ·4H ₂ O
Sodium fluoride.....	1.009	20	Same as water				Odorless	Contained 0.93% Al. sulfate
Cresol calcium.....	1.075	20	Same as water				Odorless	Contained 1.8% ZnCl ₂ Contained 8.9% sodium silicate
										Contained 1.2% sodium fluoride
										2.43% cresol calcium solution

than plus or minus ten per cent. could not be obtained in these tests, largely because of variables inherent in wood, the following conclusions should be interpreted liberally:

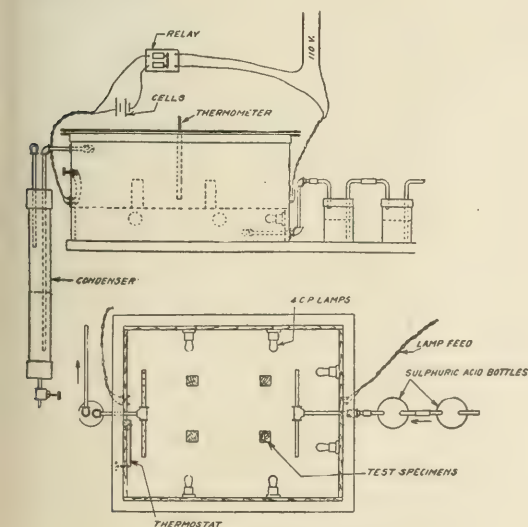


FIG. 4—VOLATILITY APPARATUS

1. All of the preserving oils, *vis.*, coal-tar creosote, hardwood tar, wood creosote, 1.07 oil, and copperized oil, produced, *per se*, no appreciable weakening in

the strength of the wood impregnated with them. The increases in strength noted in some cases were probably due to a lower moisture content in the treated specimens at the time of test. The amount of moisture which they contained could not be definitely determined although it is believed to be below six per cent.

2. In general, the water-soluble preservatives caused a slight weakening of the seasoned wood. This was most pronounced in the case of sodium silicate and by-product zinc sulfate. The values given for the effect of these preservatives are accentuated, due to the higher moisture content of the treated pieces. The application of a moisture correction factor would probably show that with the exception of sodium silicate and by-product zinc sulfate the weakening caused by these water-soluble preservatives is of no practical significance.

3. The following preservatives, so far as penetrance is concerned, can be considered satisfactory: coal-tar creosote, S. P. F. and Avenarius carbolineums, 1.07 oil, copperized oil, zinc chloride, zinc sulfate, cresol calcium, B. M. preservative, and sodium fluoride.

4. The "creosote" from Douglas fir was very difficult to force through hemlock, being about twice as resistant as coal-tar creosote.

5. Satisfactory penetrations with hardwood tar, timber-asphalt, and sodium silicate were not secured. The results indicated that they are from six to eighteen times as resistant to impregnation as the preservatives mentioned in conclusion (3).

Penetration of the Preservative into Wood (for details see Table III).

TABLE III—PENETRATION OF THE PRESERVATIVES AND THEIR EFFECT ON THE STRENGTH OF WOOD

Preservative designated by co-operator as	PENETRATION				Average absorption of preservative in per cent of modulus of rupture of untreated wood	Moisture at test		
	Rad. and Tang.		Long(a)			Untreated	Treated	
	Max.	Min.	Max.	Min.				
	In.	In.	In.	In.				
					Lbs. per cu. ft.	%	%	
Coal tar creosote.....	0.28	0.23	6.0	5.3	8.76	93	6.2	..
S. P. F. carbolineum.....	0.37	0.23	6.0	5.7+	8.83
Avenarius carbolineum.....	0.17	0.12	6.0	5.3+	8.08	109	6.81	..
Hardwood tar.....	0.03	0.03	0.92	0.50	6.50	98	6.11	..
Creosote (Douglas fir).....	0.08	0.08	3.58	2.33	2.82	107	5.8	..
1.07 oil.....	0.10	0.10	6.0	3.33	9.58	108	4.52	..
Timber-asphalt.....	0.02	0.02	0.33	0.33	5.68	106	6.68	..
Copperized oil.....	0.22	0.22	6.0	4.08	8.58	101	5.49	..
Zinc chloride.....	0.10	0.083	6.0	5.3	0.43(b)	88	7.13	9.35
Zinc sulfate (by-product).....	0.25	0.17	6.0	4.66	1.11(c)	82	3.88	5.77
Zinc sulfate.....	0.10	0.08	6.0	4.66	0.96(c)	89	5.14	9.6
Cresol calcium.....	0.10	0.10	6.0	3.30	0.46	103	5.72	6.58
B. M. preservative.....	0.13	0.10	6.0	4.6	0.50(c)	85	5.16	9.48
Sodium silicate.....	0.05	0.03	0.46	0.30	0.99	82	6.42	7.38
Sodium fluoride.....	0.10	0.10	6.0	5.00	0.20	85	5.82	8.7

(a) A penetration of 6 inches was the maximum that could be secured. The absorptions here given have no reference to the data on penetration.

(b) Dry salt. (c) For composition, see Table II.

Permanence of the Preservative after Injection into Wood (for details see Table IV).

TABLE IV—PERMANENCE OF THE PRESERVATIVE AFTER INJECTION INTO WOOD

Preservative designated by co-operator as	LEACHING					VOLATILITY									
	Per cent dry salt leached after immersion in water for					Per cent volatilized after seasoning for									
	5	10	15	20	30	10	20	30	50	70	90	10	20	30	50
	days	days	days	days	days	days	days	days	days	days	days	days	days	days	days
Coal-tar creosote.....	13	20	24	28	30	32
Coal-tar creosote, Frac. 1(a).....	13	21	26	32	36
Coal-tar creosote, Frac. 2(a).....	8	12	16	20	22
Coal-tar creosote, Frac. 3(a).....	7	10	12	15	17
Coal-tar creosote, Frac. 4(a).....	3	4	4.5	5.0
Coal-tar creosote, Frac. 5(a).....	1.8	2.5	3.0	4.0
Hardwood tar.....	11	12	13	19	20	22
Wood creosote (Douglas fir).....	11	11	17	19	20	28
1.07 oil.....	11	8	11	12	14	18
Copperized oil.....	1	2	4	6	9	11
Zinc chloride.....	46	54	57	60	62
Zinc sulfate.....	42	50	53	56	59
Zinc sulfate (by-product).....	47	57	63	65	68
Cresol calcium(b).....	21	26	28	31	33
B. M. preservative(c).....	43	47	51	54	57

(a) The volatility of these fractions are comparable only to each other. Their volatilization should not be compared with that of the other preservatives. For absorption of preservative, see Table III.

(b) Percentage of calcium; cresols not determined.

(c) Percentage of zinc chloride only.

6. After three months' exposure about one-third of the coal-tar creosote injected into the test specimens had volatilized. This was about 4 per cent more than for creosote from Douglas fir, 10 per cent more than for hardwood tar, 14 per cent more than for 1.07 oil, and 21 per cent more than for copperized oil, tested under similar conditions.

7. After one month's leaching, nearly two-thirds of the zinc chloride injected into the wood had leached. This loss was 38 per cent greater than the amount of coal-tar creosote which volatilized during the same period. It should be noted, however, that the test

for leaching was much more severe than the test for volatilization.

8. The volatility of coal-tar creosote fractions was proportional to their distillation. Fractions with low ranges, *ceteris paribus*, are less stable than those with high. At the end of one month the lowest had lost about eight times as much as the highest.

Effect of the Preservative on the Combustibility of Wood (for details see Table V).

TABLE V—INFLAMMABILITY OF TREATED WOOD

Preservative designated by co-operator as	Temperature of ignition C.		Loss in weight due to burning calculated in % of weight before ignition		CHARACTER OF COMBUSTION
	Days after impregnation		Days seasoned		
	2	90	2	90	
Untreated wood.....	320	...	29	...	Burned freely
Coal-tar creosote.....	173	216	40	27	Burned freely, black smoke, easily extinguished
S.P.F. carbolineum..	243	...	26	..	Burned like coal-tar creosote but not so freely
Avenarius carbolineum.....	213	...	32	..	Burned like coal-tar creosote but not so freely
Hardwood tar.....	190	241	29	30	Burned freely, dense black smoke
Wood creosote (Douglas fir).....	167	217	36	26	Burned like coal-tar creosote
1.07 oil.....	231	243	40	31	Burned like Avenarius carbolineum
Timber-asphalt.....	296	...	28	..	Did not burn freely
Copperized oil.....	200	228	43	33	Burned like coal-tar creosote
Zinc chloride.....		287(a)	..	19	Hard to ignite, burned poorly, easily extinguished
Zinc sulfate.....		304(a)	..	18	Hard to ignite, burned poorly, easily extinguished
Zinc sulfate (by-product).....		298(a)	..	15	Hard to ignite, burned poorly, easily extinguished
Cresol calcium.....		288(a)	..	29	Burned freely, white smoke, hard to extinguish
B. M. preservative.....		305(a)	..	18	More difficult to burn than zinc chloride
Sodium silicate.....		309(a)	..	10	More difficult to burn than B. M. preservative
Sodium fluoride.....		303(a)	..	25	Burned like zinc chloride

(a) Woods treated with salts were ignited as soon as their moisture content was reduced by air seasoning to 6%, usually about two weeks after impregnation. For absorption of preservative, see Table III.

NOTE.—All salts burned for less than three minutes. All oils burned for three minutes and were then extinguished.

9. Wood treated with the oils in every case ignited at lower temperatures than untreated wood. When permitted to air-season for three months the temperature of ignition was considerably raised, due probably to the evaporation of the more volatile constituents. The loss in weight from burning treated wood seasoned for three months was also less than in the specimens burned shortly after impregnation (exception—hardwood tar).

10. In general, wood treated with the water-soluble preservatives ignited at higher temperatures than wood treated with oils, although the temperature of ignition was lower than the untreated wood.¹ Furthermore, wood treated with the water-soluble salts showed in general a less loss in weight after combustion.

¹ Wood dipped in a 50 per cent. sodium silicate solution ignited at a temperature of 448° C. and its weight was reduced 17 per cent, although it immediately extinguished when dropped in the lower chamber of the inflammability apparatus.

tion than those treated with the oils. It should be noted, however, that the amount of wood actually burned may have been greater than in the case of oils.

11. Untreated wood and wood treated with oils (exception—timber-asphalt) burned freely and in gen-

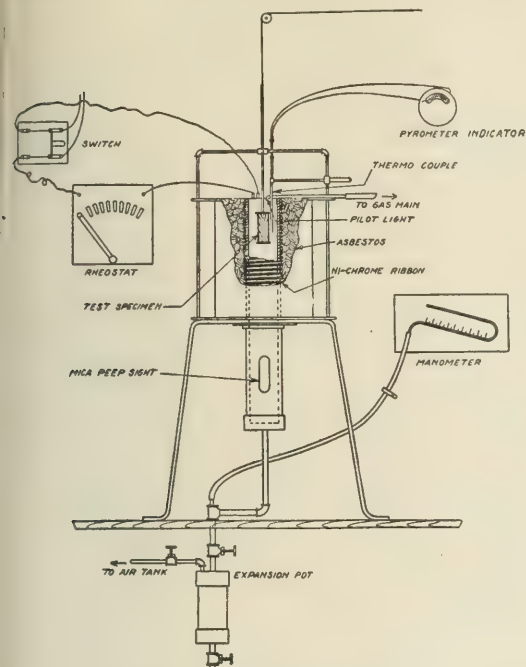


FIG. 5—INFLAMMABILITY APPARATUS

eral had to be extinguished after a 3-minute period, while wood treated with water-soluble salts (exception—cresol calcium) burned slowly and became extinguished in less than three minutes.

Toxic Efficiency of the Preservative in Inhibiting Fungus Growth (for details see Table VI).

TABLE VI—TOXICITY OF PRESERVATIVES

(As determined by the Petri-dish method against *Fomes Annosus*, Fr.) 0 = no growth. 1 = slight growth. 2 = retarded growth. 3 = strong growth

PRESERVATIVES DESIGNATED BY CO-OPERATOR AS		PER CENT OF PRESERVATIVE	
Coal-tar creosote, Fraction 1	Coal-tar creosote, Fraction 2	Coal-tar creosote, Fraction 3	Coal-tar creosote, Fraction 4
Coal-tar creosote, Fraction 5	S. P. F. carbolineum	Avenarius carbolineum	Hardwood tar
Wood creosote (Douglas fir)	1.07 oil	Timber-asphalt	Copperized oil
Fuel oil	Zinc chloride	Sapwood antiseptic	
0.2	1	0	0
0.4	0	0	0
0.6	0	0	0
0.8	0	0	0
1.0	0	0	0
2.0	0	0	0
3.0	0	0	0
4.0	0	0	0
5.0	0	0	0

(a) Creosote, Fraction 1, is so volatile that concordant results are difficult to obtain. At the close of the experiment it is probable that much of the preservative had evaporated from the medium—which may account for the low toxicity indicated.

(b) Slight growth at 75 per cent.

The following tentative conclusions on the toxicity of the various preservatives may be drawn, although the author wishes to emphasize that they should not as yet be considered final, due to errors peculiar to the Petri-dish method.

12. Zinc chloride and coal-tar creosote offered about the same resistance to the growth of a wood-destroying fungus.

13. The toxicities of the coal-tar creosote fractions distilling below 320° C. were quite similar to each other and to coal-tar creosote.

14. Those portions of coal-tar creosote distilling above 320° C. were but slightly toxic, being at least fifteen times less resistant than the creosote itself.

15. The toxicity of preservatives designated as S. P. F. and Avenarius carbolineums was quite similar, being somewhat less than that for the coal-tar creosote tested.

16. Preservatives designated as 1.07 oil, timber-asphalt, copperized oil, fuel oil, and sapwood antiseptic all had no effect in inhibiting fungous growth up to concentrations of at least one per cent.

The methods of determining toxicity by pure-culture-jar and fungus-pit tests have, up to this writing, not progressed sufficiently far to yield definite results.

Although too few determinations have been made to date to draw final conclusions, nevertheless those which have been made indicate that the ball test should prove highly valuable in determining mechanically the extent of decay in wood.

Corrosive Action of the Preservative on Flange Steel (for details see Table VII).

TABLE VII—CORROSIVE ACTION OF THE PRESERVATIVE

PRESERVATIVE DESIGNATED BY CO-OPERATOR AS	LOSS IN WEIGHT (GRAMS) OF FLANGE STEEL AFTER IMMERSION IN PRESERVATIVE AT 98° C. FOR	
	3 weeks	4 weeks
Coal-tar creosote.....	0.0064
Coal-tar creosote, Frac. 1.....	0.0000	0.0008
Coal-tar creosote, Frac. 2.....	0.0389	0.0401
Coal-tar creosote, Frac. 3.....	0.0063	0.0467
Coal-tar creosote, Frac. 4.....	0.0313	0.0296
Coal-tar creosote, Frac. 5.....	0.0005	0.0015
Avenarius carbolineum.....	0.0807	0.0951
Hardwood tar.....	8.2629	11.2350
Wood creosote (Douglas fir).....	5.0989
Spiritine.....	1.2938	1.5029
1.07 oil.....	0.0243
Timber-asphalt.....	0.2222
Copperized oil.....	0.0096
Fuel oil.....	0.0012	0.0062
Zinc chloride.....	1.4636
Zinc sulfate (a).....	0.6050
Zinc sulfate (b) (by-product).....	1.3809
B. M. preservative.....	3.1660	4.1746
Sodium fluoride.....	0.1256	0.1588
Cresol calcium.....	0.0139	0.0181

(a) Equivalent to 2.1% zinc chloride solution.

(b) Equivalent to 6.2% zinc chloride solution.

For concentration of salt solutions used, see Table II.

17. Of the various preservatives tested, coal-tar creosote and copperized oil had the least deleterious effect on steel and their action in practical operations can very probably be neglected.

18. All the metallic salts were much more pronounced in their action than coal-tar creosote, so that the

depreciation in plants using them would, unless precautionary measures were taken, be greater.

19. The very marked corrosion of hardwood tar and creosote from Douglas fir is probably due to the comparatively large amount of acetic acid which they contain.

Discoloration of Painted Wood (for details see Table VIII).

TABLE VIII—DISCOLORATION OF PAINTED WOOD

PRESERVATIVE DESIGNATED BY CO-OPERATOR AS	CONDITION OF PAINTED SURFACE AFTER EXPOSURE FOR ONE MONTH
Coal-tar creosote	Very badly discolored and paint not dry
Hardwood tar	Very badly discolored and paint not dry
Wood creosote (Douglas fir)	Very badly discolored and paint not dry
1:07 oil	Very badly discolored and paint not dry
Copperized oil	Discolored, paint somewhat sticky
Zinc chloride	Appearance similar to the untreated specimen
Zinc sulfate (by-product) ..	Appearance similar to the untreated specimen
Zinc sulfate	Appearance similar to the untreated specimen
B. M. preservative	Appearance similar to the untreated specimen
Sodium fluoride	Appearance similar to the untreated specimen

20. All of the oils tested rendered the wood unfit for subsequent painting. Copperized oil was least objectionable in this respect. If thoroughly dried after treatment so that excess oil would not appear on the surface, it is possible that wood treated with some of these preservatives could be satisfactorily painted with dark pigments.

21. The water-soluble salts were all satisfactory in that they caused no discoloration of the painted surface. If used under conditions where the wood is subjected to moist air, none of these preservatives might prove commercially satisfactory.

CONCLUSIONS

The depth to which oils can be impregnated varies as some inverse function of the viscosity. As temperature strongly influences the viscosity of oils, and as the diffusion of the preservative through the wood is one of the most important factors in proper treatment, it is concluded that to secure best results both the wood and the preservative should be heated to the proper temperature during the pressure period. Because of the low thermal conductivity of wood, the treatments should not be made too rapidly. With water-soluble salts these precautions are not important.

With coal-tar creosote it appears that the fractions of greatest stability are the least toxic. Present practice rather favors the retention in treated wood of the more volatile fractions by an admixture of the more stable ones. If the toxic values here given are correct, there is in practice being forced into wood about two and one-half times as much zinc chloride and fifty times as much coal-tar creosote as is necessary to prevent decay. It is concluded therefore, that more economic results against decay, especially when it is accompanied by mechanical deterioration, can be secured by diffusing the preservative more thoroughly through the wood than by saturating the outer fibers and attempting to retain in the wood the volatile constituents through admixtures of non-volatile constituents.

In general, the flash or burning point of an oil affects the inflammability of wood treated with it.

Of greater importance, however, is the length of time the treated wood has seasoned, as a prolonged seasoning of such wood raises considerably its ignition temperature. It is concluded that it would be good practice to first season such treated timber before placing it in positions subject to fire. While wood treated with the water-soluble salts mentioned in these tests was in general less difficult to ignite than untreated wood, nevertheless the presence of such preservatives almost invariably renders the wood slow burning and easily extinguishable.

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

THE MENHADEN INDUSTRY¹

By J. W. TURRENTINE
Received February 21, 1913

HISTORICAL

The fish scrap industry may be said to have had its inception even before the advent of white settlers on the American continent. While the industry as such did not exist at that early date, practices were in vogue which led directly to that industry. Reference is had here to the customs which existed among the American Indians of New England of fertilizing their crops by means of fish. It is stated that for fertilizing corn, one or two fish were placed in each corn hill. This practice was adopted by the colonists, and extended to the scattering of fish broadcast over the fields. In later years, where the latter was carried to an extreme, it was found that the practice resulted in serious detriment to the soil because of the accumulation therein of the undecomposed oil from the fish. Later, it was found that the oil could be easily removed from the fish without impairing their usefulness for fertilizer purposes. This was accomplished by placing the fish in hogsheds or barrels, covering with water, compressing with weighted boards, and allowing to stand for the putrefaction of the fish to release the oils. The oil rose to the surface and was skimmed off. The residue was spread upon the land. The oil thus obtained was put to various uses in the domestic enterprises of the farms. It was soon found that cooking the fish released the oil as effectually as disintegration through putrefaction, and very much more quickly and less offensively.

For the farmers living near the shore it became a part of the year's routine to prepare fish scrap and, incidentally, oil for the year's supply. As the spring was regarded as the best time for the application of this fertilizer, a few weeks of the spring were devoted to fishing and rendering. The apparatus necessary, seines and pots, were often owned and operated in common.

In time, pot-cooking was superseded by the adoption of steam cookers; the first factory for cooking by steam was a small one put up near Portsmouth, Rhode Island, in 1841.²

"In 1850 Daniel Wells built a factory on Shelter Island, New York. That was the first factory of con-

¹ Published by permission of the Secretary of Agriculture.

² Stevenson, "Aquatic Products in Arts and Industries," U. S. Fish Comm., *Ann. Rept.*, 1902, 256.

considerable size on the coast, and the quantity of fish handled amounted to 2,000,000 or 3,000,000 in number annually. In 1853 Mr. Wells built a new factory on Shelter Island, and the old one was removed to Groton, Conn., being the first steam factory in that State. The first factory in Maine was put up in 1863 at South Bristol, and in 1866 eleven factories were built in Maine. In 1869 the factory at South Bristol, Me., was removed to Fair Port, Va., and was the first factory in that State.¹

The subsequent development of the industry was marked by the introduction of the purse seine,² admitting of the capture of fish in greatly increased numbers, and the adoption of presses for separating the oil, and increasing the yield of it, in the place of the older method of depending on the lighter specific gravity of the oil to effect a separation. Hand presses were introduced in 1856, by Mr. Chas. Tuthill, of the Wells factory on Shelter Island. In 1858 hydraulic power was introduced as a substitute for hand power. In more recent years, steam presses have been introduced with such success that they are to be found in practically every new factory, and they are being rapidly installed in the old factories to take the place of those operated by hydraulic power. A further rapid development of the industry was made possible through the substitution of steamers for sailing vessels; this rendered the fisherman independent of the winds in searching for and overtaking the schools of fish and in returning to the factories with their cargoes. In spite of this self-evident advantage, it has been only within the last few years that the last sail boats of considerable size, fishing for menhaden, have been equipt with auxiliary engines.

The so-called "floating-factory" was designed to obviate the waste of time incurred by the fishing boats in going back and forth between the factories and the fishing grounds, the idea being to carry the factory to the fish instead of taking the fish to the factory. Introduced in 1876, a number had been constructed and were in operation in 1880. They consisted in boats of various sorts equipt with the apparatus for rendering the fish, such as boilers, cooking vats and presses. The lack of storage room for the products, the difficulties of loading and unloading at sea and other considerations, brought about their abandonment. The latest attempt to apply the floating factory idea was in 1911, when a steamer of 5,000 tons was equipt with a complete set of the modern automatic apparatus for producing dried scrap.³

A form of fish-scrap fertilizer, which could be shipped long distances or stored, was first prepared by drying on platforms the scrap from the presses. Here the material was spread to dry and was manipulated in the meantime by hand rakes or hoes to expose fresh surfaces. In certain instances, platform drying is still in use, notably in those neighborhoods where the odor and smoke from hot air driers lead to the hostile action of the inhabitants of the neighborhoods. However, the dispatch and convenience with which

scrap may be dried in the artificial driers have led to their almost universal adoption.

"The business continued to expand until it reached its high water mark in 1884, when 858,592,691 fish were caught, yielding 3,722,927 gallons of oil and 68,863 tons of scrap, valued at \$2,800,000. Since that time great improvements have been made in the methods of the industry, but owing to the low price of oil and scrap, resulting from the competition with other products, the profits have not been so great and many factories have been dismantled. The largest catch of fish in any one year, according to the figures of the U. S. Menhaden Oil and Guano Association, was 858,592,691, taken in 1884; the smallest was 223,623,750, secured in 1892, and the average catch during the last thirty years approximates 500,000,000 annually. The incomplete returns for 1902 indicate that the catch exceeded 900,000,000, a greater quantity than for any previous year."⁴

The literature dealing with the fish scrap industry is confined almost altogether to a small number of reports, prepared through state or federal initiative. Their fewness in number is more than counterbalanced by their excellence. Conspicuous among these are two valuable reports by G. Brown Goode, on "The Natural and Economic History of the American Menhaden,"⁵ and by Chas. H. Stevenson, on "Aquatic Products in Arts and Industries,"⁶ respectively. The present writer has drawn freely from these articles for supplementary information used in the present paper.

PRESENT STATUS

At present there are about 40 factories on the Atlantic seaboard which manufacture fish scrap. This number includes only those whose main output is fish scrap and fish oil. Thus are excluded those whose output in fish scrap is small and an entirely secondary matter, such as the concerns which manufacture glue from cod and other fish refuse. While residues from the cookers of these are sold for fertilizers and are essentially fish scrap, their output in scrap is too small to accord them more than mere mention in this discussion.

Of this number of plants, the distribution by states is as follows: Maine, 1; Connecticut, 2; New York, 3; New Jersey, 2; Delaware, 2; Virginia, 20; North Carolina, 11; and Florida, 2; from which it is seen that the Chesapeake Bay region, in point of number of plants, is the center of the industry.

In the following table are listed the factories of the principal producers of fish scrap and their location:

TABLE I—LIST OF FACTORIES OF THE PRINCIPAL PRODUCERS OF FISH SCRAP ON THE ATLANTIC COAST, AND LOCATION

NAME OF CONCERN	LOCATION OF PLANT
MAINE	
Deep Cove Manufacturing Co.,	Deep Cove.
CONNECTICUT	
Niantic Menhaden Oil & Guano Co.,	South Lyme.
Wilcox Fertilizer Co.,	Mystic.

¹ Stevenson, *Loc. cit.*

² U. S. Fish Comm., *Ann. Rept.*, 1877, pp. 1-529.

³ *Loc. cit.*

⁴ Quoted from Stevenson, *Loc. cit.*

⁵ Further discussed under "Technology."

⁶ For a description of this plant see section on "Technology."

TABLE I—(Continued)

NAME OF CONCERN	LOCATION OF PLANT
NEW YORK	
Atlantic Fertilizer & Oil Co.,	Promised Land.
Neptune Fishing Co.,	Promised Land.
Triton Oil Co.,	Promised Land.
NEW JERSEY	
Monmouth Oil & Guano Co., (Successors to the Vernon S. Vail Co.)	Port Monmouth.
New York & New Jersey Oil & Guano Co.,	Port Monmouth.
DELAWARE	
Delaware Fish Oil Co.,	Lewes.
Lewes Fisheries Co.,	Lewes.
VIRGINIA	
Bellows & Squires,	Ocran.
Coan River Oil & Guano Co.,	Lewisetta.
Carters Creek Fish & Guano Co.,	Irrington.
Davis Packing Co.,	Reedville.
Davis, Palmer Co., ¹	Palme.
Dennis Fish & Oil Co.,	Cape Charles.
The Douglas Co.,	Reedville.
The Edwards Co., ^(a)	Reedville.
The Edwards & Reed Co.,	Reedville.
The Hubanks, Tankard Co.,	Kilmarnock.
Indian Creek Fertilizer Co.,	Byrdton.
McNeal, Edwards Co.,	Reedville.
Menhaden Oil & Guano Co.,	Harborton.
Morris, Fisher Co.,	Reedville.
Norfolk Fisheries Corporation, ^(b)	Seaford.
Seaboard Oil & Guano Co., (Successors to Haynie & Snow)	Reedville.
Seaboard Oil & Guano Co., (Successors to Hinton, Tolson Oil & Guano Co.)	Mila (near Reedville).
Seaboard Oil & Guano Co., ^(c)	Chincoteague Island.
Stringfellow Operating Co., ^(d)	Harveys Wharf.
Wharton Fisheries Co., Inc.,	Ocran.
Taft Fish Co.,	Taft.
NORTH CAROLINA	
Beaufort Fish, Scrap & Oil Co.,	Beaufort.
Chadwick & Caffrey,	Beaufort.
C. P. Dey,	Lenoxville Point (Beaufort).
Doan & Bartlett,	Beaufort.
Ocean Fisheries Co.,	Wilmington.
Nat. Russell,	Swansboro (near Beaufort).
R. W. Taylor,	Morehead City.
Taylor & Guthery,	Morehead City.
Charles S. Wallace,	Morehead City.
Charles S. Wallace,	Smyrna (near Beaufort).
A. T. Willis,	Williston (near Beaufort).
FLORIDA	
Pensacola Rendering Co.,	Pensacola.
Southern Menhaden Co.,	Fulton.

(a) In course of erection, 1912.

(b) In the hands of receivers. Office at Berkeley, Va.

(c) In course of erection, 1912.

(d) Receivers for Menhaden Fishing Corporation.

The output, by states, during the year 1912, is given in the following table. The figures given in the compilation for the most part were obtained on or before Nov. 1. While the catch for the balance of the season was estimated in certain instances, it is believed that the figures here given may be low.

TABLE II—THE OUTPUT IN FISH SCRAP BY STATES, 1912

State	Tons	
	Acid	Dry
Maine.....	100	256
Connecticut.....	1,500	6,500
New York.....	19,800
New Jersey.....	530	1,500
Delaware.....	6,312	500
Virginia.....	34,000
North Carolina.....	7,250
Florida.....	160

Announcement is made of the recent organization of the following companies to engage in the fish scrap industry: The South Coast Oil & Fertilizer Co., to operate at Port Arthur, Texas, and E. E. Saunders & Company, to operate at Pensacola, Fla.

TECHNOLOGY

Fishing.—The time of fishing for menhaden is determined, of course, by the habits of the fish. Since they appear in northern waters in April and disappear in November, the fishing season is delimited by those months. As one goes farther south, the season is lengthened; in the Carolinas the boats are not put out of commission until the latter part of December, though fishing does not begin much earlier there than in the northern regions. In the southern region, the spring and fall fishing furnishes most of the raw material, there being a dull season in mid-summer when catches are rare and unimportant. In Florida waters the fish are present throughout the winter.

The range covered by the fishing boats is determined by the habits of the fish, the situation of the factory to a slight extent, and by the power and speed of the boats themselves. As the menhaden are rarely found north of Cape Cod, that point may be said to be the northernmost limit of the fishing grounds, though often in the past fish have been found farther north than that. At times big catches have been made in Cape Cod Bay and Boston harbor. The Chesapeake boats, perhaps, cover the wider range, as they habitually fish from Nantucket to Hatteras. This is determined in part by their more central location and in part by the Virginia fishing laws which prohibit boats owned by non-residents of the state from fishing in the waters controlled by the state. As most of the fish are caught within the three-mile-from-shore limit, this law rather discourages the boats of the northern fisherman from coming that far South. Since similar laws are not enforced by the other coastal states, the Virginia fisherman enjoys a range not permitted to the boats from other states. At least, the law reserves Chesapeake Bay for the Virginia fisherman.

The boats used in the fishing industry are by no means uniform in construction, though the modern boats built especially for fishing are constructed after a certain general model. Without entering into a detailed description of their lines, it may be said that in general they are constructed with a high bow and a low beam. The former adds to their seaworthiness and gives the additional advantage that from the pilot house situated thereon a wider range of vision is afforded and the schools of fish may be more readily discerned. The latter adds to the facility with which the fish may be transferred from the seines to the hold of the boat. The pilot house and quarters are situated in the bow of the boat while the engine room, boilers and bunkers are placed toward the stern, the middle portion of the boat being constructed as the receptacle for the fish. This part is provided with large hatches to facilitate loading and unloading. The arrangement is somewhat the same in the small auxiliary schooners, the galley and quarters being situated forward and the engine room aft, the hold for receiving the fish occu-

pying, again, the middle of the vessel. The larger steamers have a capacity of 750,000 fish and carry a complement of 50 men. The auxiliary sail boats have a capacity of about 250,000 fish.

Each boat carries two purse boats. These frequently are towed, being tied together and fastened in closely so that their bows touch the stern of the fishing steamer or schooner. The purse boats, so named because they are used in spreading and otherwise manipulating the purse seines, were formerly of the whale boat type, somewhat modified. They are constructed to possess the qualities of steadiness in the water, as considerable active moving about within them is occasioned by the manipulation of the seines, and of being easily towed and rowed. Formerly, they were of a lap-streak construction, but now one finds a smooth-bottom boat, with battened seams, in general use. The more flaring sides of the whale boat have given way to a straighter and more nearly perpendicular shape. The boat might be described as long, deep, and narrow. These changes are said to give greater speed, and greater durability on account of the closer seams; and the smooth sides and bottom prevent the entanglement of the twine of the seines. They are 30 to 35 feet in length and are provided with a platform, running their length, with elevations fore and aft.

The purse seine is in general use among the menhaden fishermen. Its adoption marked an important stage in the development of the industry due to its great superiority over the older forms. The seine is about 1,500 feet long by 180 feet wide. When extended in the water it is supported by a row of corks fastened along its top. The distinctive feature of the purse seine is the arrangement provided for drawing it together, purse-wise, at its bottom. At frequent intervals along its lower edge are suspended metal rings, about 3 inches in diameter (which also serve as weights to keep the seine fully stretched), through which passes a rope. The ends of this purse line are held in the purse boats. When the fish have been surrounded and the two ends of the seine brought together, the bottom of the seine is drawn together by hauling on the purse lines. This prevents the fish from escaping by diving beneath the bottom of the net. As the seine is carried partly in one boat and partly in the other, spreading it is accomplished by rowing the two boats in opposite directions, playing out the seine as the boats separate. In fishing this is done in such a way as to intercept and surround a school of fish. When the two boats have met on the side of the school opposite to that from which they started, the purse line is hauled in to draw the seine together at the bottom and the fish are secured. The seine is then hauled in to force the fish into a smaller compass. Following that, the steamer is brought alongside and the fish are dipped from the seine by means of a large dip net, operated by an arrangement of block and tackle, and emptied into the hold.

Unloading.—Unloading at the docks was formerly effected by means of tubs, filled by hand, and hoisted to the docks by means of block and tackle. This has

been supplanted at practically every factory by one or two elevators. These are bucket elevators and are an adaptation to the handling of fish of the apparatus employed in unloading wheat. The elevator is fed, partly automatically through the fish sliding toward it of their own weight, and partly through the aid of three or four members of the crew armed with shovels.

The elevator deposits the fish into an automatic measuring device which partakes of different forms at different factories. It may have the form of two bins provided with a device for diverting the stream of fish into the other when the one has secured a certain weight, the bottom of the loaded bin being opened at the same time. A form is frequently found which has the shape of a cylinder divided into segments and mounted so as to revolve horizontally on an axis. When one segment of the cylinder has received a definite weight of fish, the cylinder is revolved through an angle, a new section is brought into position to be filled and the one filled is emptied.

Measuring the catch is an important operation as upon it is based the bonus to be paid the fishermen. In the north, the captain of the steamer and perhaps his first officer are paid on the bonus basis, while in certain parts of the south, the entire crew are so compensated. While fish are rated in thousands, less frequently in barrels, actually they are not counted at all but are measured in bulk. The space occupied by a single menhaden is taken arbitrarily as 22 cubic inches; however, since they vary so widely in size the volume of an individual may be far from that. A thousand, accordingly, are considered to occupy 22,000 cubic inches; this bulk of fish, whether occupied by 500 or 2000, is rated as a thousand, weighs 666 pounds and is equal to $3\frac{1}{2}$ barrels.

From the measuring apparatus the fish are deposited in storage bins from which they are carried as needed to the cookers. The transfer may be made by cars or by automatic conveyors, depending on the equipment of the plant.

The operations so far mentioned are typical and are in vogue, with slight modifications, in practically every plant on the Atlantic coast. The subsequent treatment of the fish, however, varies widely with respect to apparatus, though it follows in general one of two methods which may be styled the old, or discontinuous method and the new, or continuous process. Due to the gradual displacement of the old apparatus by the new, all combinations of the two processes are found.

Cooking.—(Old Method.) The old method of cooking in open vats is still in vogue in such a number of factories as to justify its description here. The vats employed are usually situated on the second floor of the factory so that the mixture of oil and water subsequently to be pressed from the cooked fish can follow its prescribed course through the plant without the assistance of pumps. They are constructed of wood or cement, with a false bottom, beneath which are placed steam pipes. The individual vats may have a capacity of about 20,000 fish, and the entire set of vats, 300,000 fish. They are arranged generally in

two adjacent longitudinal rows. Above them runs the track conveying the tram cars or the automatic conveyor which supplies the fish to be cooked, while along either side of the double row are placed other tracks running to the presses.

Fish are dumped into the vats in quantities depending on the capacity of the vats, usually 50 to 100 barrels, some water is added and the steam is turned on. They are cooked about 20 minutes, or a sufficient length of time to cause them to break up easily, but not long enough to disintegrate them entirely. The object of the cooking is to break the oil cells or to bring about that condition which admits of a more ready expressment of the oil. If the cooking is too prolonged this is accomplished, also, but the flesh is so thoroughly disintegrated that it becomes a mush from which it is difficult to separate the oil: the oil, water, and fine particles of flesh would then squeeze out of the presses together.

Pressing.—(Old Method.) The cooked fish are thrown from the vats into the curbs of the presses by means of a modified shovel which retains the solid matter and permits the water to run back into the vats. The curbs are mounted on trucks and are brought alongside the vats by means of the track, spoken of above, which parallels the rows of vats. The curbs are generally tubs, whose cross section is a circle, constructed of metal slats with an outward slant. The spaces between the slats are of a suitable width to permit the water and oil to escape when the pressure is applied, but to retain the solid matter. The spaces are of the same width from top to bottom, since the outward slant of the slats is compensated for by the increased width of the slats. The bottom is hinged, and while securely fastened, its lock is readily manipulated and the bottom easily released. An iron shield is generally placed around the curb to protect the workmen from the jets of water and oil which escape from the curb when pressure is applied.

The curb, when it has received its charge of fish, is rolled back beneath the press and the power is applied. In certain of the smaller factories in the Beaufort region, screw presses, manipulated by hand, are still in use. Most of the other plants using the older, discontinuous method of expressing the fish, however, are equipt with hydraulic presses.

The escaping water and oil is caught by the properly slanting floor as is also that escaping from the curb during charging, and conveyed to the oil room for settling and further treatment. When the maximum pressure has been applied and no more liquid is being forced out, the pressure is released and the curb is rolled over an opening in the floor for emptying. The bottom is then released and swings downward, and the mass of fish scrap falls in a solid cake to the floor below. The slanting sides of the curb are designed to facilitate the discharge of this cake; the curb being larger at the bottom than at the top, the cake falls out more readily. At this stage, the scrap contains about 50 per cent. water, by weight, and about 6 or 9 per cent. of oil. In its warm and moist condition it makes an ideal breeding place for various flies and

for the growth of decay-producing bacteria. Unless it is to be immediately dried, it is treated with crude sulfuric acid ["about a dipper full (3 quarts) to a cart load"] in small but sufficient amount to discourage the development of insect and other life therein. The acid, besides acting as a preservative, brings about a disintegration of the flesh and bones of the scrap. It is claimed to "dissolve" the bone and to "fix the ammonia." It does render a larger proportion of the phosphoric acid of the bones "available" and may possibly convert some of the nitrogen of the complex organic bodies in the flesh into ammonia, to form ammonium sulfate. What is meant by this fixation probably is that the decay of the fish, leading to the loss of nitrogen or possibly to the actual liberation of ammonia, is prevented. This so-called "acidulated" or crude scrap may be sold as such, or, as opportunity presents, finally may be dried.

Drying.—(Old Method.) The old platform drier has been supplanted in almost every factory on the Atlantic coast by the modern and more rapid hot air drier. As must be inferred from the name, the platform method consists merely in spreading the scrap on a platform where it is exposed to the air and sun. The platform in some cases is built of boards raised a few inches from the ground, and in other cases is made of concrete. The scrap is frequently stirred either by hand rakes or hoes or by scrapers drawn by horses. At night, or when rain is threatened, the scrap is raked into heaps and covered by canvas. Under favorable conditions, three days' drying is required. The product obtained by this method of treatment is a much lighter brown in color than that dried by hot air. Its odor is also less marked. It is said that considerable ammonia is lost by thus exposing the scrap so thoroughly and for such a long time to the air. Whether fish scrap loses nitrogen on exposure to air when in a nearly dry condition and when no recognizable decay is taking place, is a mooted question. Experiments bearing on this point are under contemplation in this laboratory.

Cooking.—(New Method.) The new method of cooking fish largely has supplanted the old because of its speed and efficiency and the saving in labor which it effects. The apparatus employed is essentially a long, narrow, iron cylinder, of varying lengths, but frequently about 40 feet, and about 2 feet in diameter, through which the fish are passed by means of a screw conveyor, being subjected the while to the cooking action of steam. These usually are constructed for a capacity of 100,000 fish per hour and may be purchased at a cost of about \$1200.

There are several forms of this apparatus, differing from each other principally in the manner in which the steam is admitted to the cylinder. Thus, it may be admitted through perforations in the hollow shaft of the screw conveyor; the blades of the conveyor may be substituted for by sections of iron pipe, arranged screw-wise around the axis, through perforations in which the steam may enter the chamber; or it may be admitted through numerous pipes projecting from the outside through the casing along its bottom.

The second and third methods mentioned are regarded by the operators as more efficacious, as they admit the steam within the mass of fish, instead of above it, and thus effect more thorough and uniform cooking.

The fish are conveyed automatically from the storage bins and are dumped continuously into the hopper-like mouth of the cooker. This, in certain forms, is provided with a special device for regulating and assisting the feeding. The cooked fish, together with the water and oil cooked from them and the water resulting from the condensed steam, are passed from the end of the cooker into the buckets of a conveyor and are transported to the presses.

Pressing.—(New Method.) The modern power press employed in the fish scrap industry partakes of the shape of a truncated cone placed in a horizontal position. It is, essentially, a curb, constructed of iron, with slatted sides. Through its center passes a horizontal shaft on which is built up a screw, tapered to fit closely inside the cone-shaped curb. The rotation of the screw carries the fish forward into the smaller end of the curb; and as the material can not rotate with the screw, or slip on the curb, it is subjected to pressure. By adjusting the size of the opening in the smaller end, through which the expressed material is ejected, the pressure on the mass may be increased or decreased. The pressure is gradual, increasing from the larger end toward the smaller. The water and oil are squeezed out between the slats and are caught by the metal shield surrounding the press and are conducted thence into pipes leading to the oil room.

The mouth of the press is hopper-shaped. The fish are fed into this by a mechanical conveyor. In some forms of the press, a chopper is placed in the mouth to reduce the size of the pieces of fish entering. From the smaller end of the press the fish scrap usually is allowed to fall into the buckets of a conveyor.

One hundred pounds of the mass coming from the cookers contains 22 pounds of fish and 78 pounds of water. In the press, 56 pounds is removed. This leaves a mass of 44 pounds, 22 pounds of which is fish and 22 pounds water (50 per cent.).

The 18-foot power press is obtainable at a cost of \$5000, set up complete. This has a capacity of 80,000–100,000 fish per hour. A smaller press, 12 feet in length and with a capacity of 40,000 fish per hour, may be purchased, complete and set up, for \$3500.

The advantages of this system of ridding the fish of their water and oil are obvious. Its speed and the fact that it is continuous and automatic, requiring no labor, have enabled it to displace the discontinuous, hydraulic press in a number of old factories and have brought about its adoption in practically all of those recently constructed.

Drying.—(New Method.) The hot air drier is now in use in all but about four of the fish scrap factories on the Atlantic coast. In at least two of the factories it has not been adopted because of the hostility of the residents of the neighborhood occasioned by the odor rising from the factories, increased during the actual operation of the drier, and exhibited by frequent suits at law.

The modern drier is an insulated iron cylinder, about 6 feet in diameter and 30 or 40 feet in length. It is provided on the inside with a series of iron flanges or shelves, about 8 inches wide and running the length of the cylinder. These are designed to lift the scrap and spill it again through the stream of hot air. The cylinder is mounted slightly out of the horizontal and is supported by a device consisting of two jointless steel tires or rings encircling the cylinder toward either end and resting on steel rollers or wheels. These rollers are rotated by suitable gearing, driven by an electric motor, and they, in turn, impart rotation to the cylinder. Its higher end, which is the front end, enters a brick chamber, the bottom part of which constitutes a fire box. Suitable openings are provided for stoking, etc., and an electric fan is also provided to produce a forced draft. The wet fish scrap is charged at this end, being allowed to drop directly into the swift stream of hot gases entering the cylinder from the furnace. The forced draft serves also to blow the scrap through the kiln as it is repeatedly lifted and dropped in the rotation of the kiln. The finer particles, which are more quickly dried, are blown more rapidly out of the zone of fiercer heat. The movement of the scrap through the kiln is induced, then, both by the draft and by the slope of the cylinder. The lower end likewise enters a brick chamber, practically cubical in shape, designed to fill the threefold purpose of catching the scrap as it falls from the cylinder, of acting as a sort of dust-settling chamber, and of serving as a poor sort of chimney. From this chamber the scrap is conveyed, again by bucket conveyor, to the warehouse where it is stored, or ground, or bagged. The transit through the drier consumes from 3 to 20 minutes, depending on the force of the blower, the rate of rotation of the kiln and the degree of fineness of the lumps of scrap on entering the kiln. The moisture content is reduced to about 7 per cent. As some of the kilns are being operated, about 5 tons of coal per day are consumed. According to the various estimates of the operators, a million fish produce 75–85 tons of dry scrap; 12,000–15,000 fish are required to make one ton of scrap. The drier, complete and set up, may be purchased for \$3,000 inclusive of blower, bricks, etc.

The hot air drier for fish scrap is a useful piece of apparatus and its introduction marks an epoch in the fish scrap industry. It has rendered it almost altogether unnecessary to acidulate scrap since the drier is practically always able to handle the output of the cookers and presses. In the plant equipt with a full set of the improved machinery, the fish are not moved by manual labor from the time they are fed to the elevator in unloading until the dry scrap is being bagged. The whole operation requires less than an hour.

Theoretically, the hot air drier is inefficient. Theory requires that in drying, the drying agent shall be passed over the material being dried in a direction opposite to that in which that material is moving. Thus, in drying by a stream of hot air, the hottest and driest air is brought into contact with the driest material and as it becomes more heavily charged with water

vapor, passes progressively over wetter and wetter material. In this way the maximum moisture absorbing power of the air is made of use. In the drier in use in the fish scrap industry, the opposite arrangement obtains: the hottest and driest air is brought into contact with the wettest and coldest fish, and the wettest and coldest air, into contact with the driest and warmest fish. The objections raised to the former procedure is that the dried scrap is inflammable and a careful regulation of the temperature would be required to prevent the scrap from catching fire. There is little danger of this with the present scheme. However, it would be a simple enough matter to lower the temperature of the drying gases far below the ignition temperature of the dried scrap, by introducing a sufficiently large volume of cold air into the gases from the furnace; or, the fire could be largely reduced in size. Certainly the same amount of drying could be effected with a smaller consumption of coal, or, with the same consumption of coal more efficient drying and possibly, more rapid drying could be effected by the use of a larger volume of air. And equally doubtless the process could be made as automatic as the present one.

A more serious objection to the present practice in drying scrap is the undoubted destruction of a part of the scrap in the drying. As was stated, the wet scrap is dropped directly into the white-hot gases from the furnace. The scrap as it enters is in the form of lumps varying in size from the smallest particles to masses several inches in diameter. With a heat intense enough to dry the larger lumps in a maximum of 20 minutes, it is evident that the finest particles must be utterly consumed. The greater speed with which they travel must save much of that in the form of the less fine particles. This is an *a priori* conclusion, but is practically indisputable. Whether the loss is serious or not can not be said until more experimental evidence is adduced.

The combustion of the fish is further attested by the odor of the smoke which emerges from the "stack" of the drier. This is a heavy smoke, largely mixed with steam and distillation products, and smelling to heaven with the odor of scorched flesh. It carries also numerous fine particles of scrap, which in the course of a year's run, must represent a considerable loss. The odor, while unbearable to a novice, is not objected to by those who are used to it; in fact, they declare a liking for it, since to them "it smells like money."

In certain neighborhoods where the majority of the residents are not in sympathy with the industry, the hot air driers are not used at all, or if used, are operated only at night or when the wind is off-shore. A tall stack, while an expensive adjunct to a plant, would to a considerable extent alleviate this objection to the use of the drier.

Grinding and Bagging.—After drying, it remains only to bag and ship the fish scrap. Some scrap is shipped in bulk, being transferred by conveyor directly to the hold of the transporting vessel. Much is bagged without further treatment; some is ground to a meal before bagging. For the ground scrap a

slightly higher price is obtained, representing little more than the cost of grinding. In certain mills, the scrap is mixed ("manipulated") with phosphate and potash carriers to produce a so-called complete fertilizer, and is thus marketed under brand names. Other companies are planning an extension of their present operations in that direction. In certain other instances the scrap is shipped to manipulating plants owned and operated by the fish scrap company. In all other cases, with the exception of the small amounts used locally and as chicken feed, the scrap is shipped directly to the producers of finished fertilizers.

The Factory.—In locating a factory for the manufacture of fish scrap an attempt is made to obtain a combination of deep water, protected harbor and nearness to fishing grounds. An effort is made further to find a location that is sufficiently isolated to obviate the danger of litigation on the grounds of being a nuisance because of odors at times created at the plant. Since fish are almost invariably unloaded from vessels of considerable tonnage and draft, proximity to a water course of sufficient depth is essential to permit the fishing boats to approach their docks. In the case of most of the plants, docks of only moderate length have been required. In one instance, the entire factory has been built over the water.

The elevators and other hoisting and unloading devices are situated on the ends of the docks. The storage bins likewise may be built on the docks, though more generally they are to be found closer to the factory. If the former, they are so situated with respect to the elevator that they are supplied directly from the measuring apparatus forming a part of the elevator; if the latter, they are fed by cable cars or automatic conveyors. The bins are situated at such an elevation that the fish after leaving them again do not have to be raised to any considerable height. In agreement with this arrangement, the cookers and presses are placed on the second floor of the factory, the cooker at a greater elevation than the press, and the drier on the ground floor.

The equipment of the average factory consists of one dock, elevator, bin, cooker, press and drier, with a capacity for the factory of about 100,000 fish per hour. The largest factory on the coast has 2 cookers, each of 500 barrels per hour capacity and 6 presses. The usual rate of operation of this plant is 600-900 barrels fish per hour. It has produced oil at the rate of 75 barrels per hour.

Besides the equipment mentioned there is required also a steam and power plant to supply steam for the cookers and oil boilers and to furnish power for driving machinery. For the average plant, of one working unit, a boiler capacity of about 300 horse power is adequate. Certain plants generate their own electric power, and at least one has installed separate electric motors for driving the various pieces of apparatus with moving parts.

Capacious storehouses are provided to hold the dried scrap. These are usually built as a separate part of the plant to reduce fire risks and often are

capable of holding the season's output. Bagging, usually done by hand at times when the rest of the plant is lying idle, is carried on in this building. The output of a plant is determined, not by its capacity but largely by the number and success of the boats fishing for that plant. The average number of steamers operated by a factory is about three. One company operates 27 steamers, 11 of which carry their catches to one factory, while certain manufacturers depend for their supply entirely on the fish sold to them by fishermen working independently. The price of raw fish varies from season to season and month to month; during the summer of 1911, \$2.25 per 1000 was paid, while during 1913, raw fish brought only \$1.50 per 1000. Since so much depends on the fortunes of the fishermen, the supply of fish is uncertain and irregular. No plant runs constantly at capacity. Some may stand idle for months in the midst of the fishing season. The fish are worked up as received. This is especially necessary in warm weather, when the fish, often bruised and softened by the crushing produced from their own weight, are sure to spoil rapidly. Accordingly, the factories are operated intermittently. A much higher daily capacity is maintained therefore, than would be necessary in handling a raw material of a more permanent character, or one supplied with greater regularity.

The Floating Factory.—The perfection of the automatic apparatus for handling fish scrap with dispatch has been followed by another attempt to manufacture scrap in a vessel capable of following the menhaden during the season. In July, 1911, the "Mills" was put into commission. This steamer is a converted steel dredge, of 5,000 tons, which has been equipped with two elevators, one on each side, with a capacity of 1,500 barrels of fish per hour. These deposit the fish into receiving bins of 5000 barrels capacity. A continuous and automatic cooker is provided and a rotary press. Storage room, with adequate fire protection, is reserved for the dried and bagged scrap, and likewise storage tanks capable of holding as much as 3,000 barrels of oil. A wireless outfit is also a part of the equipment.

MENHADEN OIL

Development.—Menhaden oil, the true fish oil, and by far the most important oil produced on the Atlantic coast of the United States, first appeared on the market in considerable quantity in the early 60's. The large prices obtained in the early days of the industry led to a rapid development in the industry and a consequent overproduction in oil. In the 70's the annual production exceeded 2,000,000 gallons, a figure which it has closely maintained on the average ever since.

Prices.—The range in prices since 1863 of crude northern oil is given in the subjoined table. The data for the years 1863 to 1902 are taken from the report by Stevenson, previously quoted from, those for the following years from the *Oil, Paint and Drug Reporter*. The southern oil is regarded as inferior to the northern and fetches a somewhat lower price.

During the past year the oil has varied in price from 23 cents to 28 cents per gallon.

TABLE III.—STATEMENT OF THE RANGE OF PRICES FOR CRUDE NORTHERN MENHADEN OIL IN THE NEW YORK MARKET FROM 1863 TO 1910, INCLUSIVE

Year	Lowest	Highest	Year	Lowest	Highest
1863	\$0.75	\$1.00	1888	\$0.20	\$0.32
1864	1.10	1.35	1889	0.21	0.32
1865	0.80	1.40	1890	0.22	0.30
1866	0.70	1.135	1891	0.255	0.30
1867	0.45	0.70	1892	0.30	0.38
1868	0.50	0.95	1893	0.33	0.40
1869	0.625	1.025	1894	0.21	0.33
1870	0.40	0.68	1895	0.19	0.25
1871	0.35	0.55	1896	0.18	0.23
1872	0.36	0.65	1897	0.18	0.25
1873	0.32	0.605	1898	0.225	0.24
1874	0.35	0.475	1899	0.225	0.72
1875	0.305	0.485	1900	0.25	0.27
1876	0.30	0.50	1901	0.26	0.30
1877	0.30	0.46	1902	0.26	0.29
1878	0.23	0.45	1903	0.22	0.27
1879	0.24	0.35	1904	0.21	0.25
1880	0.29	0.43	1905	0.17	0.21
1881	0.30	0.395	1906	0.24	0.26
1882	0.32	0.42	1907		
1883	0.35	0.48	1908	0.24	0.27
1884	0.26	0.475	1909	0.21	0.30
1885	0.21	0.30	1910	Contract(a)	Contract(a)
1886	0.20	0.26	1911		
1887	0.19	0.21			

¹ Sold by contract. No quotations.

Technology.—The mixture of oil and water running from the cooked fish in the presses is conducted into the first and uppermost of a set of tanks, arranged one somewhat above the other. In this vat the mixture on standing a short time separates into a stratum of oil floating on an aqueous layer. The separation may be assisted by heating the mixture. For this purpose steam coils are provided. The oil is allowed to flow thence by a suitable arrangement of wiers successively through the series of receptacles, in which by means of stronger heating by steam it is gradually purified from its contained water and small particles of flesh. The greater part of the fine particles of flesh separate in the first vat, settling to the bottom. This fine mush is known as "gurry," and sometimes is sold to the manufacturers of soap without further treatment, and in some cases is placed in stout canvas bags and subjected to pressure to recover the oil which it still contains. The residual solid matter is added to the scrap. As this is free from bones, its nitrogen content is correspondingly higher than that of the ordinary scrap.

The oil that has been put through the simple process of separation and purification described is run directly into barrels for shipment or into large storage tanks from which it is drawn off as desired for shipment. It usually is sold in bulk to oil refiners by whom it is prepared for the various uses to which it is adapted.

Yield.—The yield in oil varies (1) with the year, (2) more decidedly with the locality from which the fish are taken, and (3) most widely with the time of the year when taken. The fish taken in northern waters as a rule are fatter than those from southern waters. "In the year 1900, for instance, the yield of oil at the Rhode Island factories was 5.76 gallons per 1,000 fish; in New York it was 6.39 gallons; in Delaware, 4.92 gallons; and in Texas, 3.51 gallons to the 1,000 fish."¹ When the fish appear in the spring they frequently

¹ Stevenson, *loc. cit.*

are so thin that no recoverable oil at all is obtained from them. The fish taken in the fall, on the contrary, yield on the average 12 gallons per 1,000 and frequently 15 gallons per 1,000. The variation in average yield per thousand from year to year, therefore, probably is determined by the relative number of fish caught in the spring and fall.

Properties and Uses.—Crude menhaden oil varies in color from light amber to dark brown. This wide range in color is due to the variation in the manner of treatment of the fish and the preliminary purification of the oil. Its viscosity is determined largely by temperature.

Formerly menhaden oil was used principally as an illuminant and in currying leather. In addition, it has long been used as a paint vehicle, as a lubricant and as a soap-making grease. Its use in currying leather and as an illuminant has been supplanted to a considerable extent by that of mineral oils, while its employment in the other manners mentioned has increased. Large and increasing quantities now are used in the paint manufacturing industry, and in tempering steel. For the latter purpose a large amount is sold directly to the manufacturers of steel articles.

Important contributions to the knowledge of fish oils as paint vehicles have been made by Toch.¹ This paint and oil specialist regards menhaden oil as the best of the fish oils. He differentiates strictly between menhaden oil and other so-called fish oils such as those obtained from the whale, porpoise and seals, as those from the latter three sources lack those qualities, possessed by menhaden oil to a marked degree, which would classify them as drying oils. Their admixture with drying oils such as tung and boiled linseed oils does not avail, for, while they may appear to have dried, they become sticky again in the presence of heated air.

It is recommended that, for exterior work, three parts of fish oil be mixed with one part of linseed oil. The mixture is non-hygroscopic—when dry it remains dry—and the results obtained with it are described as excellent and lasting. The iodine number, it is maintained, is an index of the suitability of fish oils for paint purposes. It may be substituted for linseed oil profitably in a number of applications. It is more resistant to the action of heat than linseed oil and hence is especially adaptable to use in painting iron work such as boiler fronts and smoke-stacks. It holds up better in a moist climate, such as that existing in proximity to the seashore. Its use is recommended especially for replacing linseed oil in the manufacture of patent leather and similar products, and printing ink. The patent leather resulting is more flexible and less liable to crack, though it possesses a somewhat less glossy surface. An objection to its use in this manner, however, is a peculiar efflorescence which its presence causes to form on the surface of the preparation. Its moderate use in the manufacture of baked japans also has been found highly advantageous.

"Menhaden oil should, of course, be used with a drier, and for that purpose the best results are obtained

by means of a Tungate drier. A Tungate drier is one in which tung oil or China wood oil is boiled with a lead and manganese oxide, and when the solution is complete this is then mixed with a properly made resinat of lead and manganese. Such a drier becomes soluble in the oil at temperatures over 100° C., and hardens the resulting paint very thoroughly. For fabrics, however, fish oil must be heated to a temperature of over 200° C., and if air is injected at such a temperature the glycerides are expelled and thick oil is produced which, in conjunction with the drier just named, is equally good for printing inks. It is advisable, however, to add at least 25 per cent of either a heavy bodied linseed oil or a raw linseed oil which does not break before the manipulation just referred to is begun."¹

The manipulation requisite on the part of the manufacturers to render their oils immediately usable for paint vehicles involves merely the addition of the drier and boiled linseed oil to the fish oil. The product should be sold directly to the paint manufacturers. The advantages gained are a higher price gotten because of this manipulation and because of the elimination of the middleman, and the assurance which the paint manufacturer has that the oil purchased directly from the manufacturer of fish oils is probably the pure product.

In this connection it should be added that undoubtedly there are certain other ways, and probably many more, in which the value of the menhaden oil might be easily enhanced. The considerable portion of the time, when, because the fish-rendering plant is lying idle, the employees are unoccupied should make it possible for the operators to expend more labor on their oil, with a view to the improvement of its quality, and to manipulate it to render it suitable for special purposes, without greatly adding to the cost of manufacture.

USES OF FISH SCRAP

As Fertilizer.—Fish scrap from the inception of the industry has met with great success as a fertilizer, until to-day it constitutes one of the main sources of the organic nitrogen used in the fertilizer industry. Its nitrogen is in a form from which it readily is rendered available by the bacterial and other action taking place in the soil. The organic matter, which serves as the carrier for the nitrogen in fish scrap, as in other organic nitrogenous substances is a beneficial adjunct to this fertilizer not enjoyed by the inorganic nitrogenous substances.

A small amount of fish scrap is used directly as a fertilizer, without admixture with other fertilizer ingredients or fillers. Its success when used alone has not been unequalled. Its continued application has led to a condition of the soil in which the soil would no longer respond to that fertilizer. A larger portion is mixed ("manipulated") by the manufacturers of the scrap to form a so-called complete fertilizer and is sold, generally, locally, under brand names. During the past year (1912) about 10,000 tons were thus employed. This practice is growing.

¹ Toch, *THIS JOURNAL*, 3, 627 (1911).

¹ Toch, *Loc. cit.*

By far the larger portion of the output of the east is sold directly or through the medium of brokers, to the larger manufacturers of fertilizers by whom it is worked up into the various grades of finished goods marketed by them.

As Chicken Feed.—This use of fish scrap at present is so slight as scarcely to deserve mention. Only a few tons, and these by a small number of chicken growers, are thus utilized; but the success of those so using it, evidenced by their yearly increasing orders, would seem to justify its exploitation by experiment stations and its trial by other poultry raisers.

The following paragraph is quoted, with excisions, from Goode:¹

"At a meeting of the Maine Board of Agriculture and Farmers' Convention, Mr. Wasson gave an interesting account of the use of 'porgy chum'² as a food for sheep and poultry, stating that he had used it for five years. * * * Sheep thus fed showed an average increase each of one pound and a quarter of wool, while they were constantly fat and brought heavy lambs. Hens also ate the scrap with avidity. Boyd stated that hens, ducks, and turkeys preferred it to corn, and became large and heavy when fed upon it. It is customary to discontinue the scrap and feed them on corn three or four weeks previous to killing them."

As Cattle Feed.—The use of fish scrap as a feed for cattle has met with such success, seemingly, in those instances where it has been tested that it is surprising that its adoption for this purpose has not become more general. In Shetland and Iceland, it is reported, dry, salt fish constitute the main feed for cattle and sheep, and is even fed to horses.

"The most rational method of utilizing fish for manure, and the one which it seems to me must prove by far the most profitable way of economizing our waste fish products, is by feeding them to stock."³

The following paragraphs are quoted from a paper by Atwater, which has been published as a part of the report by Goode:

"The earliest accounts which I have met of fish as food for domestic animals is the following extract from the Barnstable (Mass.) 'Journal,' of February 7, 1833:

"The cattle at Provincetown feed upon fish with apparently as good relish as upon the best kinds of fodder. It is said that some cows, kept there several years, will, when grain and fish are placed before them at the same time, prefer the latter, eating the whole of the fish before they touch the grain."

"In 1853, Mr. J. B. Lawes, of Rothamsted, England, reported several extensive series of experiments 'On the Feeding of Pigs,' in which were tested the effects of beans, lentil, Indian corn, and barley meals, bran, and dried Newfoundland codfish as foods for fattening. * * * In speaking of the series in which the fish was fed with maize, barley, and bran in different proportions, Mr. Lawes says:

"In the series * * * where we have * * * a comparatively small amount of non-nitrogenous matter consumed, the food consisted in a large proportion of the highly nitrogenous codfish; and in both of these cases, we had not only a very good proportion of increase to food consumed, but the pigs in these pens were very fat and well ripened. * * * This result is in itself interesting, and it may perhaps point to a comparatively greater efficiency in the already animalized protein compounds supplied in the codfish than in those derived, as in the other cases, from the purely vegetable diets."

"The value of fish as food for domestic animals has been attested by experience of intelligent farmers in our own country. As early as 1864, if not in fact previous to that date, the attention of members of the Board of Agriculture (of Maine), and Farmers generally was called to the value of fish pomace or scrap as a feeding stuff for sheep, swine, and poultry. In a communication to the Board¹ Mr. William D. Dana, of Perry, spoke in high tones of its value as a feed for domestic animals, in which he said: 'Fish pomace, or the residuum of herring after the oil is pressed out, is greedily eaten by sheep, swine, and fowl; and probably 'porgy chum' would be eaten as well. Smoked alewives and frost fish also furnish a food palatable to cattle. Sheep thrive well, get fat, and yield heavier fleeces when fed on this pomace than when fed on anything else produced in this section of the State. Careful and observing farmers, who have fed it, assert that * * * its value for manure is in no degree diminished by passing it through the living mill, thus reducing it to a much more convenient state for applying. If it could be sufficiently dried, without other substances, to prevent putrefaction, it would form a valuable article of cattle feed in regions from which it is now excluded by the expense of transportation and its own odoriferous nature.'"

It is apparent that the scrap spoken of here as used in these feeding experiments is the undried scrap as taken from the presses. No reason suggests itself why the dried scrap should not be as nutritious as the wet as, theoretically, the drying causes no chemical change in the organic substances of the scrap, but merely removes water. The advantages of the dry over the wet scrap as a feed are numerous and great.

Feeding experiments were conducted by Farrington at the experimental farm of the Maine College of Agriculture. Two flocks of lambs, of five each, were chosen and during a period of sixteen weeks one flock was fed corn and hay and the other fish scrap and hay. During the first four weeks of the experiment, "the corn-fed flock, weighing 340 $\frac{1}{2}$ pounds, ate 335 pounds of hay and lost 19 pounds in weight. The flock eating fish, weighing 338 pounds, ate 338 pounds of hay and lost 1 $\frac{1}{2}$ pounds." During the sixteen weeks of the experiment, the sheep were fed about 2 ounces of fish scrap per head per day, and the same amount of corn; in that time the corn-fed flock gained 48 pounds, or 15 $\frac{1}{8}$ per cent., and the fish-fed flock 47 $\frac{1}{2}$ pounds, or 15 $\frac{1}{16}$ per cent. As the fish scrap was unground

¹ "History of the American Menhaden," *Rept. U. S. Fish Comm.*, 1877, 140-1.

² By "porgy chum" is meant the crude and undried fish scrap.

³ Goode, *Loc. cit.*, p. 248.

¹ *Agriculture of Maine*, 1864, p. 43.

and contained bones, it was not entirely eaten.

"On the whole, then, these experiments [and others] described in the report by Atwater but omitted here] bear unanimous and convincing testimony in favor of the easy digestibility and high nutritive value of animal foods in general and of fish guano in particular when fed to sheep and swine. How far they could be made profitable for other herbivorous animals than sheep has not yet been tested. In the nature of the case there is no reason why they should not be as nutritious for neat cattle as for sheep. As Voit has justly observed, all mammals are at one period of their lives, when living upon milk, carnivorous. * * *

"In short, we have every reason, from practical experience, from actual experiment, and from what we know of the nature of the case, to believe that the immense amount of animal waste produced in this country from our slaughter houses, and especially from our fisheries, can be utilized with the greatest ease and profit to supply the most pressing need of a most important part of our agriculture, nitrogenous food for stock."

"The ingredients of fish may be made more available for plant food and their value for manure increased by * * * feeding to stock, thus putting it through a process similar to that by which Peruvian guano has been formed. In this way it can be used to enrich the manure made on the farm, and thus made one of the best aids to successful farming."

Concerning the utilization of fish scrap as cattle feed, Henry, in 'Feeds and Feeding' says:

"*Dried Fish*.—Along the coasts of Europe the waste parts of fish, as well as of fishes not used for human food, are fed in dried form to animals. Spier of Scotland reports no bad influence on milk when reasonable quantities of dried fish are fed to dairy cows. Nilson found that 80 parts of herring cake could replace 100 parts of linseed cake in the ration for cows. The better grades of dried fish meal should be used for feeding farm animals.

"*Flesh Meal, Fish Scrap*.—In a trial by Schrodt and Peters, bran and rape cake were gradually replaced by equal quantities of flesh meal until the allowance of the latter reached 2.2 pounds per head daily. It was found that the customary shrinkage in live weight when in full milk flow did not occur, and there was an increase in the total quantity of milk as well as in the total solids and fat. Flesh meal effected a saving of 2 lbs. of feed per head daily, and the cows learned to relish it highly.

"According to Kuhn, milk and butter of normal quality were produced on a daily allowance of 2.3 lbs. of fat-free fish scrap supplied with a variety of other feed, no deleterious effects resulting."

The universally affirmative results of all the recorded experiments with fish scrap as a cattle feed leaves little room for doubt as to its efficiency. It is, indeed, surprising that its use as a feed has not been

more generally introduced. This is doubtless due to the lack of exploitation on the part of the manufacturers, the ones most vitally interested financially.

It will be recalled that in the beginning of the cotton-seed oil industry, the expressed cake was a by-product which found use only in the fertilizer industry. Its subsequent exploitation as a cattle feed gave it a much enhanced value. To-day it is produced in immense and constantly increasing quantities, and the portion of it which enters the mixed fertilizer is much less than the amount used as cattle feed. We venture to predict that, in that particular, the history of fish scrap will parallel that of cotton-seed meal; that the time will soon come when it will be recognized by both manufacturer and farmer that its preparation and use as a cattle feed is more profitable to both than when employed only as a stimulation for growing plants. And fitting, indeed, it would be that even a small part of the millions of pounds of combined nitrogen carried seaward annually by the rivers should be returned and, after a short cycle, again be rendered suitable for man's consumption.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

SOME ANALYSES OF FISH SCRAP¹

By J. R. LINDEMUTH AND E. G. PARKER

Received March 13, 1913

A small number of samples of fish scrap were taken, for the most part in person, by J. W. Turrentine, of this Bureau, during the fall of 1912. No attempt was made to obtain a complete series from all the plants of the Atlantic coast, but those obtained may be regarded as typical. The samples were gotten from open heaps of scrap in the storage houses, or from bags by means of samplers, or by opening the bags. They were shipped in canvas sample sacks. Before analysis, the entire sample was ground to a powder that would pass a sieve of 16 apertures per linear inch.

Methods of Analysis.—Samples of 2 grams were dried to constant weight in an electric oven at a temperature of about 100° C. The loss in weight was recorded as moisture. In this connection it should be said that it is believed that possibly some oil also was lost in this operation. Oil was determined by extracting with carbon tetrachloride a 2-gram sample, previously dried to constant weight. For the extraction a Soxhlet apparatus was employed. Following the extraction, the sample was again dried to constant weight and the loss taken as oils. In the determination of nitrogen, the official, modified Gunning method was applied, and in that of phosphoric acid, the official gravimetric method was used. The results are recorded in the subjoined table. The eleventh analysis is reported in this table merely for convenience. It is the analysis of pulverized crab shells used as a filler for mixed fertilizers. The particular adaptability of this material for that purpose is brought out by the analysis.

¹ By Wolff, Wildt, Kellner, and Weiske, described in "Die Landwirthschaftlichen Versuchs-Stationen," "J. f. Landwirthschaft" and "Landwirthschaftliche Vahrbücher," 1876 and 1877.

² Note inserted by writer, J. W. T.

¹ Published by permission of the Secretary of Agriculture.

TABLE I

No.	LOCATION	DESCRIPTION	Nitrogen		Phos. (P ₂ O ₅)		Moisture		Oils	
			Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
1	Kilmarnock, Va.	From Eubanks Tankard Co. Dry scrap (from 6 sacks)	8.93	6.17	6.48	5.91				
2	Taft, Va.	From Taft Fish Co. Dry scrap (sample from 525 tons)	8.96	7.75	6.18	6.81				
3	Irvington, Va.	From Carter's Creek Fish Guano Co. Dry scrap, dried in hot air and steam driers (from one sack) Fall product	7.70	5.22	11.68	6.62				
4	Cape Charles, Va.	From Atlantic Fish & Oil Co. Dry scrap, ground (from 3 sacks)	9.29	6.12	7.86	5.38				
5	Cape Charles, Va.	From Atlantic Fish & Oil Co. Dust from grinders	8.80	5.21	7.17	7.55				
6	Beaufort, N. C.	From Beaufort Fish-scrap & Oil Co. Dry scrap, hydraulic presses, sample from heap	8.22	5.95	6.13	8.57				
7	Morehead City, N. C.	R. W. Taylor. Dry scrap from open heap	8.49	5.95	9.12	8.23				
8	Morehead City, N. C.	From Chas. S. Wallace. Scrap, dry, from hydraulic presses	7.76	9.65	8.15	7.56				
9	Lenoxville, N. C.	From C. P. Dey. Ground scrap, sun dried, hydraulic presses. Sample from heap	7.81	5.85	7.46	7.89				
10	Lenoxville, N. C.	From C. P. Dey. Scrap, dry, ground, hydraulic presses. Sample from heap	8.29	9.00	7.00	5.40				
AVERAGES ON MOISTURE-FREE FISH SCRAP			9.13	7.25	0.00	7.09				
11	Crisfield, Md.	From L. E. P. Dennis & Son. Ground crab shells, used as filler	3.82	4.55	6.95	2.11				

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

THE EFFECT OF TEMPERATURE, ACID CONCENTRATION AND TIME ON THE BROMINATION OF PHENOL FOR QUANTITATIVE DETERMINATIONS

By L. V. REDMAN, A. J. WEITH AND F. P. BROCK

Received February 26, 1913

The rapid introduction into commerce of synthetic plastic resistives made from phenol and compounds containing mobile methylenes has made the rapid and accurate determination of phenols of great importance. This paper deals with the simplest of the series, C₆H₅OH, and will be followed later by methods for the determination of the higher homologues.

The fact that seventy-two investigators have contributed research papers on the determination of phenols is indicative of the trouble experienced in making accurate assays of phenol. Previous investigators have worked upon the theory that the bromination of phenol is a slow rate reaction and requires time for completion. To this end they have employed small volumes of rather concentrated solutions, with considerable excess of bromine during the bromination period. The result is a precipitate of tribromophenol, dense, and almost granular in structure, having often the yellow color of the tribromophenolbromide or containing the separate red specks of tetrabromophenone. As these products¹ are not completely reduced by hydriodic acid, the determinations often varied by one or more per cent.

A complete bibliography of the earlier work is to be found in Lloyd's paper² and references to the more recent investigations are found in the researches of Wilkie.³

Recently, Rhodes and Redman³ have shown that if the concentration of the phenol be approximately *N*/100 during the bromination period, the precipitate is a light flocculent, white mass through which the solution can diffuse easily and as a consequence on thorough shaking the reaction is completed in one minute's time; there is no rapid return of the blue color after titration, such as Koppeschaar mentions as incident at times in his method; and from their numbers as published the results are accurate to two or three parts in a thousand. These authors have shown that Lloyd's hypobromite and the bromide-

bromate method (Koppeschaar's solution) are equally rapid, accurate, and satisfactory, under proper conditions of acidity and phenol concentration, in forming the white, flocculent, insoluble tribromophenol. The hypobromite solution is shown to have the disadvantage of being unstable when not carefully sealed or kept in air-tight bottles, and as a consequence requires restandardization every day. The diluting of the phenol solution has entirely prevented the influence of the yellow tribromophenolbromide and the formation of the red tetrabromophenone, which have been noted as sources of error by earlier investigators.¹ Errors from these sources were consequently avoided.

There remains, however, to perfect a method for determining phenol, an investigation into:

(a) The effect of acid concentration during the bromination period.

(b) The length of time required for the liberation of the iodine by the bromine.

(c) The necessary excess of free bromine to be used.

(d) The effects of temperature.

(e) The excess of potassium bromide necessary in the bromide-bromate solution.

The only equipment required for the investigation was a mechanical shaker,² several half-liter ground-stoppered bottles and standardized burettes.

The solutions used were as follows: *N*/10 sodium thiosulfate, *N*/10 bromide bromate, *N*/10 phenol, 20 per cent potassium iodide, hydrochloric acid (sp. gr. 1.2) and a starch solution made by stirring 5 grams of starch into a liter of water, heating slowly until a clear solution is obtained, and allowing the gelatinous material to settle out.

The thiosulfate solution was prepared by dissolving 125 grams of sodium thiosulfate (Na₂S₂O₃·5H₂O) in 5 liters of water; 2.76 grams of potassium bromate and 43 grams of potassium bromide per liter of solution constituted the bromide-bromate solution; a later solution in which the potassium bromate was 2.76 grams per liter but the bromide was reduced to 15 grams per liter was found to be quite as satisfactory as the 43 grams per liter. The higher bromide content was introduced in the earlier methods to prevent the formation of tribromophenolbromide,³ but in the dilute solutions is quite unnecessary, as is shown later in this paper. The phenol solution was made from the

¹ Jour. Am. Chem. Soc., **27**, 16 (1905).

² J. Soc. Chem. Ind., **30**, 398 (1911); **31**, 208 (1912).

³ THIS JOURNAL, **4**, 655 (1912).

¹ Beckurts, Arch. Pharm., **5**, 24, 561 (1886); J. Soc. Chem. Ind., **5**, 546 (1886).

² THIS JOURNAL, **4**, 656 (1912).

³ Lloyd, Jour. Am. Chem. Soc., **27**, 15 (1905).

third distillate at 181–2° C. of Merck's c. p. phenol, 1.56 grams being dissolved and made up to one liter.

The 20 per cent KI solution was made by dissolving 200 grams of KI in 800 cc. of distilled water. The solution was not made up fresh each day as is frequently recommended. A liter of the solution required only a few drops of *N*/10 thiosulfate to reduce the free iodine which was formed in the solution during three weeks.

THE EFFECT OF ACID CONCENTRATION

In each of the following tables the order from left to right is the order in which the solutions were added for the determinations. The tables in each case show the amount of water added for dilution, the amount of acid added and the resulting normality reckoned for the total volume after the addition of the bromide-bromate solution, *i. e.*, the acid concentration during the bromination period. The excess bromine calculated and observed are given, and are expressed in percentages of the amount of bromine required to form tribromphenol of all the phenol present in the solution. The length of time given for the bromination, or the "reaction period," is expressed in minutes, as is also the time given to liberate the iodine from the potassium iodide by the excess bromine. The amounts of 20 per cent potassium iodide solution added and the amounts of thiosulfate used for titrating back the free iodine are expressed in cubic centimeters and the final column gives the percentage of phenol found in each experiment.

TABLE I—ACID CONCENTRATION

Water, 50 cc.					Reaction period for Br, 1 min. Time to liberate I, 3 min.					
Expt. No.	HCl		Phenol sol. Cc.	Br sol. Cc.	Per cent excess of Br		KI sol. Cc.	Na ₂ S ₂ O ₃ Cc.	Per cent of phenol found	
	Cc.	Nor- mality			Cal.	Obs.				
1	1	0.16	15.00	15.00	1.6	69.0	1	10.35	31.47	
2	1	0.16	15.00	15.00	1.6	60.5	1	9.07	40.77	
3	1	0.16	15.00	15.00	1.6	14.0	1	2.07	87.58	
4	1	0.16	15.00	15.00	1.6	4.4	1	0.65	97.21	
5	2	0.32	14.97	15.28	3.6	6.5	1	1.20	97.09	
6	2	0.32	14.99	15.27	3.5	5.7	1	0.87	97.70	
7	2	0.32	14.98	15.27	3.5	4.8	1	0.75	98.37	
8	3	0.48	15.00	15.00	1.6	1.4	1	0.21	100.20	
9	3	0.48	15.00	15.00	1.6	1.5	1	0.22	100.10	
10	4	0.64	15.00	15.00	1.6	1.7	1	0.25	99.91	
11	4	0.64	15.00	15.00	1.6	1.7	1	0.26	99.88	
12	5	0.64	24.90	25.00	1.9	1.9	1	0.49	100.00	
13	5	0.64	24.95	25.00	1.7	1.8	1	0.44	99.97	
14	6	0.96	15.00	15.00	1.6	1.5	1	0.23	100.08	
15	6	0.96	15.00	15.00	1.6	1.6	1	0.23	100.03	
16	7	1.12	15.00	15.00	1.6	1.6	1	0.24	100.00	
17	7	1.12	15.00	15.00	1.6	1.7	1	0.26	99.88	
KI.....			20 per cent sol.			Thiosulfate.....			0.1 <i>N</i>	
HCl.....			1.2 sp. gr.			Br.....			0.1 <i>N</i>	
Phenol sol.....			0.09843 <i>N</i>			Temp.....			22° C.	

The results in Table I show very clearly that the solution must have an acid concentration of at least 0.48 *N*, if the bromination is to be complete in one minute's time. An increase in acidity from 0.48 *N* to 1.12 *N* does not, in any way, affect the results. Later, Table V will show that the weaker acid solutions are quite satisfactory if speed is not required, in other words if a longer reaction period than one minute be allowed, complete bromination may be effected in acid solution less than 0.48 *N*.

As an increase of the acid¹ to 10 per cent does not affect the accuracy of the results by freeing a measurable quantity of iodine from the hydriodic acid during the determination, 0.84 *N* acid is recommended as a safety factor for securing rapid and accurate results.

THE EFFECT OF POTASSIUM IODIDE AND TIME

Table II deals with the length of time and the amount of potassium iodide required to reduce the excess free bromine in the solution with the simultaneous freeing of a proportional amount of iodine. In Experiments 18, 19, 20, 21, the amount of 20 per cent KI solution added was only 0.1 cc. or about 100 per cent more than is required to reduce the excess bromine present. The time given for the potassium iodide to reduce the excess bromine and liberate the iodine was one minute in Experiments 18 and 19, and 3 minutes in Experiments 20 and 21.

TABLE II—POTASSIUM IODIDE AND TIME

Water 50 cc.			Reaction period for bromine, 1 minute							
Expt. No.	HCl Cc.	Phenol sol. Cc.	Br sol. Cc.	Per cent excess of Br		KI Cc.	Time to liberate iodine Cc.	Na ₂ S ₂ O ₃ Cc.	Per cent of phenol found	
				Calc.	Obs.					
18	5	14.99	15.28	3.5	3.4	0.1	1	0.49	100.1	
19	5	14.99	15.28	3.5	3.4	0.1	1	0.50	100.1	
20	5	14.99	15.28	3.5	3.7	0.1	3	0.55	99.82	
21	5	14.97	15.28	3.7	3.8	0.1	3	0.55	99.95	
22	5	14.97	15.28	3.7	3.9	0.5	1	0.57	99.80	
23	5	14.98	15.28	3.6	3.8	0.5	1	0.56	99.81	
24	5	14.98	15.91	7.9	7.7	0.5	3	1.12	100.20	
25	5	14.99	15.91	7.9	7.7	0.5	3	1.14	100.12	
26	5	14.99	15.28	3.5	3.4	1.0	1	0.53	100.05	
27	5	14.99	15.28	3.5	3.5	1.0	1	0.52	100.00	
28	5	14.99	15.28	3.5	3.4	1.0	2	0.53	100.05	
29	5	14.99	15.28	3.5	3.4	1.0	2	0.53	100.05	
30	6	24.90	25.00	2.0	2.0	1.0	3	0.49	100.00	
31	6	24.95	25.00	1.8	1.8	1.0	3	0.44	99.97	
32	6	20.00	20.04	1.8	1.8	5.0	3	0.35	100.02	

KI..... 20 per cent sol. Thiosulfate..... 0.1 *N*
HCl..... 1.2 sp. gr. Br..... 0.1 *N*
Phenol sol..... 0.09843 *N* Temp..... Approx. 22° C.

In every case the determination is within 0.2 per cent, which is within the limit of error for the reading of the three burettes. Excess of potassium iodide above 0.1 cc. had no effect upon the determination of the free bromine. Three minutes' shaking to free the iodine gave results which did not vary from the one-minute determinations. This is not in agreement with Rhodes and Redman's statement that an error of 0.5 per cent. may be introduced with only a minute's shaking after adding the potassium iodide. As no account was taken of temperature in their experiments (laboratory temperatures), it is probable that the 1/2 per cent error which they record as due to incompleteness in the freeing of the iodine in one minute may be more properly attributed to incomplete bromination due to low temperatures in the laboratory.

THE EFFECT OF EXCESS BROMINE

Table III records the effect of excess bromine during the bromination period. The experiments show that the phenol present is changed quantitatively into tribromphenol in one minute's time, without any large excess of bromine, if the proper dilution, acidity and temperatures be observed, *e. g.*, in Experiments

¹ Lloyd, *Jour. Am. Chem. Soc.*, 27, 24 (1905).

33 and 34, 2 per cent excess bromine was used and the reaction was quite complete. Larger amounts of excess bromine (*i. e.*, up to 30 per cent) had no effect upon the determinations.

TABLE III—EXCESS BROMINE										
Water, 50 cc.			Reaction period for bromine, 1 minute Time to liberate iodine, 1 minute							
No. of expt.	HCl Cc.	Phenol. sol. Cc.	Br sol. Cc.	Per cent. excess of Br		KI sol. Cc.	Na ₂ S ₂ O ₃ Cc.	Per cent of phenol found		
				Cal.	Obs.					
33	6	24.95	25.00	1.8	1.8	0.1	0.44		99.97	
34	6	20.00	20.04	1.8	1.8	0.1	0.35		100.02	
35	5	14.99	15.28	3.5	3.4	0.1	0.49		100.10	
36	5	14.99	15.28	3.5	3.4	0.1	0.50		100.10	
37	5	14.98	15.91	7.9	7.7	0.5	1.12		100.20	
38	5	14.99	15.91	7.9	7.7	0.5	1.14		100.12	
39	5	14.98	18.29	12.4	12.1	0.5	1.78		100.10	
40	5	14.99	19.10	29.5	29.4	0.5	4.36		100.12	
KI..... 20 per cent sol.			Thiosulfate.....					0.1 N		
HCl..... 1.2 sp. gr.			Br.....					0.1 N		
Phenol..... 0.09843 N			Temp.....					22° C.		

It may be noted, however, in determining unknown solutions that the bromide-bromate solution must be added until a slight yellow color, indicating free bromine, remains permanently after shaking. This generally necessitates 5 to 7 per cent excess bromine, if the yellow color is to be seen easily. To one accustomed to the method, 2 per cent. excess bromine can be detected. The smaller the amount of bromine in excess the less will be the possible loss from evaporation and such great care is not necessary in preventing the escape of free bromine.

THE EFFECT OF TEMPERATURE

The effect produced upon the determinations by changes of temperature when the bromination period is one minute is shown in Table IV.

TABLE IV—CHANGE OF TEMPERATURE										
Water, 50 cc. HCl, 5 cc.				Reaction period for Br, 1 min. Time to liberate iodine, 1 min.						
No. of expt.	Phenol sol. Cc.	Br sol. Cc.	Per cent excess Br sol.		KI sol. Cc.	Na ₂ S ₂ O ₃ Cc.	Temp. at end of titration	Per cent of phenol found		
			Calc.	Obs.						
41	14.99	15.25	3.2	12.5	1.0	1.84	2° C.	90.88		
42	15.00	18.46	25.0	37.4	5.0	5.52	2° C.	87.66		
43	15.00	18.46	25.0	27.3	5.0	4.03	2° C.	97.74		
44	14.97	15.28	3.8	16.7	1.0	2.41	2° C.	87.34		
45	14.98	15.28	3.5	3.9	0.1	0.60	17° C.	99.56		
46	14.99	15.28	3.5	4.0	0.1	0.60	17° C.	99.50		
47	14.99	15.28	3.5	3.9	0.1	0.57	18° C.	99.63		
49	14.98	15.28	3.6	4.0	0.1	0.60	18° C.	99.56		
50	14.99	15.28	3.5	3.4	0.1	0.49	22° C.	100.10		
51	14.99	15.28	3.5	3.4	0.1	0.50	22° C.	100.09		
52	14.98	15.26	3.5	3.3	0.1	0.49	26° C.	100.20		
53	14.98	15.26	3.5	3.3	0.1	0.50	27° C.	100.10		
54	14.99	15.28	3.4	3.3	0.1	0.49	30° C.	100.10		
55	14.99	15.28	3.5	3.1	0.1	0.46	33° C.	100.40		
56	14.98	15.28	3.5	3.0	0.1	0.44	34° C.	100.62		
57	14.98	16.55	12.3	11.0	1.0	1.61	39° C.	101.30		
58	14.98	15.28	3.5	1.2	0.1	0.17	54° C.	102.45		
KI.....			20 per cent sol.		Thiosulfate.....			0.1 N		
HCl.....			1.2 sp. gr.		Br.....			0.1 N		
Phenol.....			0.09843 N							

At 2° C. the bromination is not complete in one minute and no precipitate of tribromophenol is formed. (Later experiments in Table VI will show that at 2° C. complete bromination is effected only after fifteen minutes' shaking.) At 17° and 18° the results are still one-half per cent low with the one minute's

shaking. For temperatures ranging from 22° C. to 30° C., the results are very satisfactory and accurate. Above 30° C. the amount of phenol determined is too high. This error is due to increased activity of the iodine at the higher temperatures in oxidizing the thiosulfate and tetrathionate to sulfate.¹

COMBINED EFFECT OF ACID AND TIME

In Table I, it was shown that the concentration of the acid in the solution during bromination must be at least 0.48 N if the reaction is to be complete in one minute. In Table V, it is evident that the weaker acid concentrations will effect complete bromination if a longer reaction period be allowed.

TABLE V—ACID AND TIME										
50 cc. water.			Time to liberate iodine, 1 minute							
No. of expt.	HCl		Phenol sol. Cc.	Br sol. Cc.	Per cent excess of Br		Re-action-period for Br	KI sol. Cc.	Na ₂ S ₂ O ₃ Cc.	Per cent of phenol found
	Cc.	Normality			Calc.	Obs.				
59	1	0.16	15.00	15.00	1.6	14.0	1.0	1.0	2.07	87.54
60	1	0.16	15.00	15.28	3.5	11.1	7.5	1.0	1.69	92.45
61	1	0.16	15.00	15.28	3.5	3.7	15.0	1.0	0.53	99.83
62	1	0.16	14.98	15.28	3.7	3.7	15.0	1.0	0.51	100.03
63	2	0.32	14.99	15.27	3.5	5.7	1.0	1.0	0.87	97.70
64	2	0.32	15.00	15.28	3.5	3.7	2.5	1.0	0.54	99.84
65	2	0.32	15.00	15.28	3.5	3.5	5.0	1.0	0.52	99.97
66	2	0.32	15.00	15.30	3.7	3.4	5.0	1.0	0.50	100.23
KI.....	20 per cent sol.			Thiosulfate.....					0.1 N	
HCl.....	1.2 sp. gr.			Br.....					0.1 N	
Phenol.....	0.09843 N			Temp.....					22° C.	

If the acid concentration is 0.16 N the reaction requires 15 minutes for completion, while the reaction is complete in 5 minutes if the acid concentration be increased to 0.32 N.

COMBINED EFFECT OF ACID AND TEMPERATURE

The experiments recorded in Table VI indicate that the bromination of the phenol is not complete in 0.8 N acid in one minute's time if the solution is kept at 2° C. Fifteen minutes' shaking is required at this low temperature to complete the reaction. In these low-temperature experiments a precipitation of the tribromophenol did not begin until the solution had been shaken for three minutes.

TABLE VI—REACTION PERIOD WITH STRONG ACID AT LOW TEMPERATURES										
50 cc. water, 5 cc. HCl			Time to liberate iodine, 1 minute Temperature at end of titration, 2° C.							
No. of expt.	Phenol sol. Cc.	Br sol. Cc.	Per cent ex- cess Br sol.		Re- action period for Br	KI sol.	Na ₂ S ₂ O ₃ Cc.	Per cent phenol found		
			Cal.	Obs.						
67	14.99	15.28	3.3	12.5	1	1	1.84	90.88		
68	15.00	15.28	3.5	5.3	5	1	1.00	98.27		
69	15.00	15.28	3.5	4.1	10	1	0.60	99.41		
70	15.00	15.28	3.5	3.4	15	1	0.50	100.10		
KI.....			20 per cent.		Thiosulfate.....			0.1 N		
HCl.....			1.2 sp. gr.		Br.....			0.1 N		
Phenol.....			0.09843 N.		Temp.....			22° C.		

Tables V and VI show that the two principal factors in completing the bromination of the phenol in one minute's time are acid concentration and temperature. The temperature should be roughly 20–30° C. and the acid concentration 0.5 N to 1.0 N.

EXCESS BROMIDE IN BROMIDE-BROMATE SOLUTION

A standard bromide-bromate solution (Koppeschaar's solution) consists of 2.76 grams of potassium

¹ Wright, *Chem. News*, 21, 103.

bromate and 43.1 grams of potassium bromide per liter. According to the reaction:

$$\text{KBrO}_3 + 5\text{KBr} + 6\text{HCl} = 6\text{KCl} + 3\text{Br}_2 + 3\text{H}_2\text{O}$$

2.76 grams of potassium bromate require 9.8 grams of potassium bromide, consequently the amounts stated above give an excess of 340 per cent of bromide.

Such a large excess of potassium bromide seemed to the authors unnecessary in this method, although it has been pointed out by S. J. Lloyd¹ that the rate of formation of tribromphenol bromide is decreased by the addition of potassium bromide. A bromide-bromate solution was, therefore, made up containing 2.76 grams of potassium bromate and 15 grams of potassium bromide per liter, giving an excess of 50 per cent of potassium bromide over that required by the above equation.

TABLE VII—EXCESS BROMIDE IN THE BROMIDE-BROMATE SOLUTION

50 cc. water, 5 cc. HCl.					Reaction period for Br, 1 minute Time to liberate iodine, 1 minute						
No. of expt.	HCl			Phenol sol. Cc.	Br sol. Cc.	Per cent excess		KI sol. Na ₂ S ₂ O ₃ Cc.	Per cent of phenol found		
	H ₂ O	Nor- mality	Br sol. Cc.			Br sol.					
						Cal.	Obs.				
71	50	5	0.8	15.00	15.20	3	3	0.1	0.42	100.1	
72	50	5	0.8	15.00	15.20	3	3	0.1	0.44	99.9	
73	50	5	0.8	14.99	15.19	3	3	0.1	0.44	99.9	
74	50	5	0.8	15.00	16.47	12	12	0.1	1.67	100.1	
75	50	5	0.8	15.98	17.74	12.7	12.7	0.1	1.99	100.1	

KI..... 20 per cent sol. Thiosulfate..... 0.1 N
HCl..... 1.2 sp. gr. Br..... 0.1 N
Phenol..... 0.09843 N Temp..... 22° C.

The results recorded in Table VII show that a decrease of 290 per cent in the excess potassium bromide does not affect the accuracy of determinations by this method. The tribromphenol precipitate was of the same flocculent nature as that from the bromide-bromate solution with the higher potassium bromide content, and in no instance was there a yellowish tinge, indicative of tribromphenol bromide, in the white precipitate. The results in the table show that if any tribromphenol bromide was formed it was quantitatively reduced by the free hydriodic acid.²

It may be mentioned that if one overshoots with the thiosulfate back titration by the use of the bromide-bromate solution directly, should not be practiced. The free bromine oxidizes the thiosulfate and tetrathionate to sulfate and errors amounting to 22 per cent of the quantity of bromide-bromate solution used for back titration may be introduced.

To avoid the necessity of a standard iodine solution for back titration, we have used the following method and have found it both accurate and convenient: To 10 cc. of water in a test tube, add 1 cc. of hydrochloric acid, 4 or 5 drops of bromide-bromate solution, carefully measured from the burette, a few drops of 20 per cent solution of potassium iodide, and as soon as the iodine is liberated, wash the liquid from the test tube into the determination bottle. If a sufficient quantity of the bromide-bromate solution has been taken, the blue starch iodide color is at once restored, and titration with the thiosulfate can be continued to an accurate end point.

¹ Jour. Am. Chem. Soc., **27**, 15 (1905).

² Lloyd, Jour. Am. Chem. Soc., **27**, 15 (1905).

DIRECTIONS

(1) Solutions required are 0.1 N sodium thiosulfate (24.8 grams per liter); 0.1 N bromide-bromate (2.76 grams KBrO₃ and 15 grams KBr per liter); 20 per cent potassium iodide and 0.5 per cent starch solution. The bromide-bromate solution must be compared with the sodium thiosulfate by adding acid and potassium iodide and titrating the iodine set free.

(2) Into a 500 cc. bottle, fitted with a ground glass stopper, put 50 cc. water, 5 cc. hydrochloric acid (sp. gr. 1.2) and then add 15 cc. of the unknown phenol solution which is to be determined and which has been diluted to approximately 0.1 N. If the solution is weaker than 0.1 N, no previous dilution is necessary.

Add, while shaking slowly, enough 0.1 N bromide-bromate solution to give the solution in the bottle a slight yellow color which remains permanently. The temperature of the liquid at this point should be about 22° C. Place the stopper in the bottle, giving it a sharp twist to bring the surfaces firmly together and shake continuously for one minute.

Remove the stopper, add to the solution in the bottle 0.5 cc. potassium iodide solution (20 per cent), replace the stopper and again shake continuously for one minute.

Wash down the stopper and sides of the bottle and titrate the solution with 0.1 N sodium thiosulfate, using starch solution as indicator. The starch solution should not be added until enough sodium thiosulfate has been run in to make the solution almost colorless. It is well, before the blue color of the starch iodide has entirely disappeared, to replace the stopper and shake the bottle vigorously. Care should be taken not to overshoot the end point and a standard of tribromphenol in water with excess of sodium thiosulfate should be at hand for comparison. As a further precaution the solution may be left a faint blue as less error is introduced in this way than by titrating to colorless with the attendant danger of overshooting. In case of overstepping the end point, a solution containing free iodine should be used for titrating back. If a solution containing or yielding free bromine be used for back titrating, concordant results are not obtained.

The difference between the quantity of sodium thiosulfate used and the known quantity of bromide-bromate solution added, gives the amount of bromide-bromate used up in the formation of tribromphenol. Each cubic centimeter of 0.1 N bromide-bromate solution is equivalent to 0.0015675 gram phenol.

SUMMARY

1. The results show that phenol may be determined rapidly by bromination to within an error of 0.0005 gram.

2. The quantities of reagents for determining phenol as generally recommended have been decreased without sacrificing either speed or accuracy:

(a) Two per cent excess of free bromine is sufficient for the complete bromination of phenol in 1 minute in an acid solution 0.8 N at 22° C.

(b) A large excess (over 50 per cent) of potassium iodide above that necessary for complete reduction

of the free bromine according to their equation is not required.

(c) It has been shown that not more than 50 per cent excess potassium bromide over that called for by the equation at the top of p. 392 need be used in making the standard bromide-bromate solution. The U. S. P. recommends an excess of 340 per cent.

3. Complete liberation of the iodine by the free bromine may be effected in one minute, if thorough diffusion be obtained by sufficient shaking.

4. The acidity of the solution in which the tribromophenol is precipitated must not fall below 0.48 *N* if the bromination is to be complete in one minute. An acidity of 0.5–1.0 *N* is recommended.

5. Low temperatures have a retarding influence on the rapid formation of tribromophenol: 20–30° C. is recommended.

DEPARTMENT OF INDUSTRIAL RESEARCH
UNIVERSITY OF KANSAS
LAWRENCE

PETROLEUM ANALYTICAL METHODS¹

By S. P. SADTLER

The object of this paper is to discuss the following: Can the presence of oxygen in petroleum and asphalts be established by a direct method of ultimate analysis?

To get the full import of this question, a few words of introduction are needed, bearing upon the subject of what those interested in the chemistry of petroleum and asphalt know with regard to this matter of the presence of oxygen in substances of these two classes.

Hofer² gives a list of 59 ultimate analyses of petroleum from all countries. It is true that more than half of these are the earlier analyses of St. Claire Deville and Boussingault in which only carbon and hydrogen were determined and the balance needed to make 100 was assumed to be oxygen, but in a large number of more recent analyses both the sulfur and the nitrogen when present have been directly determined and the balance then ascribed to oxygen. Notably in Russian oils and Japanese oils, both analyzed in recent years and noting the sulfur and nitrogen, has this presence of oxygen been recorded.

Rakusins³ also quotes more recent analyses of Russian petroleum by Charitschkoff and by Nastjukoff, who find from 0.4 to 2.5 per cent of oxygen and what is of interest, note that the percentage of oxygen increases in the heavy petroleum and residues with the specific gravity.

But we are not obliged to base our belief on the presence of oxygen in petroleum on calculations made from ultimate analyses. The discovery of the petroleum acids by Hell and Medinger in Roumanian oils and phenols and of the naphthene-carboxylic acids by Markownikoff and Oglobin has given us an explanation of the presence of oxygen and justified the assumptions made from the ultimate analyses.

With the natural asphalts, the case is different from that of petroleum. Although earlier ultimate analyses of asphalts gave large percentages of oxygen,

it was because the presence of sulfur in them had not been recognized and the oxygen was supposed, with the carbon and hydrogen, to make up the ash-free bitumen. However, Köhler⁴ gives several analyses of natural asphalts by Day and Bryant and by Kayser, in which a small percentage of oxygen is given as present along with a larger percentage of sulfur.

Both Clifford Richardson and Prof. S. F. Peckham, eminent American authorities on asphalt, have taken the position that not only is sulfur a distinctive element for natural asphalts, but equally that oxygen is to be considered as foreign to natural asphalts.

Besides the natural asphalts, we have also to note the artificial asphalts, obtained from petroleum, either by simple removal of the volatile portions or by some form of treatment with oxygen or sulfur at high temperatures. To the first class belong such products as "D grade asphalt,"⁵ made from California asphaltic petroleum, and "Baku Pitch"⁶ and to the second class Ventura Flux, Byerlite and Sarco asphalt. Of these last mentioned products, Byerlite and Sarco asphalt have been made from liquid petroleum-residuum by the action of a current of air, either drawn through or forced through at temperatures ranging from 380° F. (193.3° C.) to 500° F. (287.7° C.).

The action of the heated air may have two different effects⁴ according to temperature and rapidity or quantity of air passed through. The oxygen may cause splitting off of hydrogen in the form of water, with condensation of the hydrocarbons affected, or the oxygen may be fixed, forming products of oxidation which remain, in either case resulting in thick semi-solid or solid products. Not only would it be very desirable from a scientific point of view to determine which of these reactions has taken place, or whether both have united in the formation of the solid asphalt-like products obtained, but the matter has been the subject of investigation in connection with patent litigation over rival processes.

Of course, direct determinations of carbon, hydrogen, sulfur and nitrogen may and do leave varying deficiencies to be charged up to oxygen, but it would be desirable to be able to confirm these calculations by a direct determination of the oxygen in the product. No such method has thus far come into common use. The method of Baumhauer, either in its earlier form or in its later form, using a weighed quantity of dry silver iodate and requiring first a current of hydrogen, then of nitrogen and finally of hydrogen again, has not been favorably commented on by those who have tried it. The method of Mitscherlich of burning with mercuric oxide is also intended to give the oxygen at the same time that the carbon and hydrogen are obtained, but this method does not seem to have worked satisfactorily in the hands of those who have referred to it and has not been adopted by chemists.

The process which I desire to present to those in-

¹ Paper presented at the Eighth International Congress of Applied Chemistry, before the Section on Fuels and Asphalt, Sept. 6, 1912.

² *Das Erdöl und seine verwandten*, 2te Auf., Seiten 55 und 56.

³ *Die Untersuchung des Erdöls und seine Produkte*, 1906, 77.

⁴ *Chemie und Technologie der natürlichen und künstlichen Asphalte*, 1904, 81.

⁵ Clifford Richardson, "The Modern Asphalt Pavement," [2] 1908, 263.

⁶ *Ibid.*, 271.

⁷ Höfer, p. 85.

terested in this subject is very simple in theory, although its execution is not free from difficulties and requires time for its proper completion. It is primarily the invention of Dr. Wm. M. Cross, City Chemist of Kansas City, Mo., with whose permission I have worked upon it with a view to making it applicable to this class of products, and to whose courtesy I am also indebted for the permission to give publicity to these results. It consists in a combustion carried on in a current of dried and purified hydrogen gas, the front of the combustion tube being filled with iron wool, which, brought up to a bright glow and thoroughly reduced by the hydrogen, then acts as contact-substance and brings about complete reaction between the hydrogen and the vapors given off from the decomposing petroleum or asphalt, whereby any oxygen present is taken up in the form of water vapor, passing on to be absorbed ultimately in a weighed chloride of calcium tube. In making the determination, hydrogen is passed very slowly through strong sulfuric acid, calcium chloride and over phosphorus pentoxide into the end of the combustion tube containing the boat with the weighed asphalt sample, beyond which is a sufficiently long layer of iron wool. The combustion tube at the farther end is connected with a good-sized U-tube containing purified asbestos wool or preferably spun glass and this to a weighed chloride of calcium tube for absorbing water. When the combustion furnace is first lighted, only that part of the tube containing the iron wool is strongly heated, the part containing the asphalt being kept cool. Hydrogen is then passed very slowly through the apparatus until the chloride of calcium tube used for collecting water has come to constant weight and so remained for some time. The part of the tube containing the asphalt is then increased in temperature very gradually until ultimately the boat and its contents are heated to the maximum temperature attainable and so held for a time. If the large U-tube containing the asbestos or glass-wool is kept cool, no condensable vapors pass beyond, and if the current of hydrogen be continued a sufficient length of time after the full heat has been applied, it will take all water through as vapor into the weighed chloride of calcium tube. No trouble need be anticipated from the small amount of sulfur contained in the asphalt or petroleum product, because the heated iron wool is capable of taking it up, in whatever form it is liberated.

After beginning my trial of the process with ordinary combustion tubing, I was led by reason of the necessity of keeping the portion of the tube containing the boat with the weighed asphalt cool, while the portion containing the iron wool had to be heated to a bright red heat, to try a tube of fused silica and have found this to possess great advantages. With a tube of transparent fused silica, some 30 inches in length, which I obtained from the Silicate Syndicate, Ltd. of London, Eng., the iron wool can be brought to the desired heat, while the end of the tube containing the boat can be kept perfectly cool by water trickling upon it. By this means the rubber corks, with which the

ends of the combustion tubes are fitted, can also be kept cool so that no overheating can take place.

I have not yet completed my analytical work upon the material taken to try out the method and prefer to reserve a complete illustration of the applicability of the method to both petroleum and asphaltic substances for a fuller paper. I will, however, give two oxygen determinations in a blown petroleum-residuum, or so-called artificial asphalt.

Determination of oxygen	I	II
Weight of material taken	1.0065 gram	0.9767 gram
Water absorbed in CaCl_2 tube . .	0.0440 gram	0.0394 gram
Corresponding weight of oxygen . .	0.0391 gram	0.0350 gram
Percentage of oxygen	3.88 per cent.	3.58 per cent.

39 SOUTH TENTH STREET
PHILADELPHIA, PA.

EVAPORATION TEST FOR MINERAL LUBRICATING AND TRANSFORMER OILS¹

By C. E. WATERS

Received March 17, 1913

A year ago the difficulty in obtaining concordant duplicate determinations of the percentage of loss by evaporation when certain mineral oils were heated was forcibly impressed upon the writer. It was not until quite recently, however, that any attempt was made to determine to what extent the amount and rate of evaporation are influenced by conditions to be described below.

The results obtained with a typewriter oil and with two transformer oils finally led to the present work being done. The results lead to the conclusion that the factor of prime importance is, for a given temperature, the area of oil surface exposed to the atmosphere. Even when quite different weights of oil are heated in vessels of the same size, the actual losses are nearly equal, so that when the results are figured as percentages they are far from concordant. As far as we have been able to find from the literature, comparatively little attention has been paid to this factor and, indeed, to the whole subject of the evaporation of oil.

Gill² uses filter paper, $1\frac{5}{8}$ inches in diameter with a five-eighths inch hole in the center. The paper is dried in a desiccator over sulfuric acid, weighed on a watch glass and then "about 0.2 gram" of oil is dropped upon it.

We have found that eight small drops of a certain oil was sufficient to saturate the paper. This amount of oil weighed from 0.1401 to 0.1506 gram.

Holde³ uses the inner cup of the Pensky flash-point apparatus. The cup is filled to the mark and the amount of oil determined by weighing. With this cup, heated in the bath devised by Holde, it should be easy to duplicate results very exactly with a given oil. Since the loss in weight of oil depends so largely on the surface, it might seem that duplicate determinations of the percentage loss would not agree exactly if great care were not taken to fill the cup to the mark. As a matter of fact a variation of 1 mm. in the depth of the oil makes a difference of a little more than 2.0 cc. and, therefore, of rather less than 2.0 grams. The

¹ Published by permission of the Director of the Bureau of Standards.

² "Oil Analysis," 6th ed., p. 35.

³ *Mitt. techn. Vers.-Anstalt, Berlin*, 20, 67-70 (1902).

standard transformer oil of the General Electrical Society of Berlin¹ has the specific gravity 0.8825 and does not lose more than 1.0 per cent. on heating to 170° for two hours. Assuming the actual loss in weight to be the same in both cases, a difference of 1 mm. in the depth of the oil causes a difference in the percentage loss of only 0.03 per cent.

Considerable differences in the specific gravities of two oils, assuming that they both lose the same amount when heated, cause only slight variations in the percentage losses. If the oil of specific gravity 0.8825 loses 1.0 per cent. in weight, and one of specific gravity

must necessarily depend on the rate of change of the air in the oven. He devised an apparatus in which the oil is heated in a current of air or of steam, flowing at a constant rate and previously heated to the temperature of the bath. The oil (0.5 gram) is placed in a platinum dish, 3 inches long, $\frac{1}{2}$ inch wide, and $\frac{1}{4}$ inch deep. The heating bath is somewhat complicated.

Since the object of the work described in this paper was chiefly to determine the differences in the amounts of evaporation when a given weight of oil was heated with a greater or less surface area exposed to the atmosphere, a set of tubes was made from thin brass tubing

TABLE I—EVAPORATION OF OIL "A" AT 110°
Weight taken, 5.00 grams

TUBE	A	B	C	D	E	F	G	H	I	J
Diam. and depth, cm.....	2 x 3	2 x 3	2 x 5	2 x 5	3 x 3	3 x 3	4 x 3	4 x 3	5 x 3	5 x 3
Loss in 3 hrs., mg.....	8.5	8.8	8.1	8.2	8.7	9.0	9.7	10.3	11.5	11.4
Loss, per cent.....	0.17	0.18	0.16	0.16	0.17	0.18	0.19	0.21	0.23	0.23
Loss in 5 hrs. more, mg.....	1.7	1.6	0.8	0.8	3.8	3.7	5.7	6.0	10.4	9.0
Loss, per cent.....	0.03	0.03	0.02	0.02	0.08	0.07	0.11	0.12	0.21	0.18
Loss in 6 hrs. more, mg.....	1.2	1.4	0.3	0.4	2.9	3.8	6.2	5.8	Lost	9.4
Loss, per cent.....	0.02	0.03	0.01	0.01	0.06	0.08	0.12	0.12	0.19
Total loss, mg.....	11.4	11.8	9.2	9.4	15.4	16.5	21.6	22.1	29.8
Total loss, per cent.....	0.23	0.24	0.18	0.19	0.31	0.33	0.43	0.44	0.60

0.8925 loses the same, the percentage loss in the latter case is 0.989 per cent. These figures are based on the dimensions of a new cup, 51.4 mm. in inside diameter, with the mark 35 mm. from the bottom.

The chief objections to the use of the Pensky cup are its weight and the considerable amount of oil needed.

Schreiber² first used the apparatus of Holde, but later³ employed bacteriological culture dishes, "80 to 85 mm. in diameter and 20 mm. high." Here is

with bottoms of thin sheet brass soldered on. The tubes were commercial sizes having inside diameters of 2, 3, 4 and 5 cm., respectively. Tubes both 3 and 5 cm. in depth were made.

The tubes, containing weighed amounts of oil, were heated in an aluminium air bath covered with sheet asbestos. They rested on a plate of aluminium, about 3 mm. thick, to distribute the heat more uniformly. There were four ventilating openings in the bottom of the bath and two in the top.

TABLE II—EVAPORATION OF OIL "A" AT 110°
Weight taken, 5.00 grams

TUBE	A	B	C	D	E	F	G	H	I	J
Diam. and depth, cm.....	2 x 3	2 x 3	2 x 5	2 x 5	3 x 3	3 x 3	4 x 3	4 x 3	5 x 3	5 x 3
Loss in 3 hrs., mg.....	9.0	8.9	7.9	8.8	9.4	9.4	10.3	10.1	11.8	11.4
Loss, per cent.....	0.18	0.18	0.16	0.18	0.19	0.19	0.21	0.20	0.24	0.23
Loss in 5 hrs. more, mg.....	1.7	1.3	0.6	0.3	2.1	3.3	6.1	4.9	10.7	10.4
Loss, per cent.....	0.03	0.03	0.01	0.01	0.04	0.07	0.12	0.10	0.21	0.21
Loss after 6 hrs. more, mg.....	Lost	1.4	0.8	1.1	3.3	3.2	5.3	6.1	8.8	11.6
Loss, per cent.....	0.03	0.02	0.02	0.07	0.06	0.11	0.12	0.18	0.23
Total loss, mg.....	11.6	9.3	10.2	14.8	15.9	21.7	21.1	31.3	33.4
Total loss, per cent.....	0.23	0.19	0.20	0.30	0.32	0.43	0.42	0.63	0.67

Averages, Tables I and II..... 0.23

0.19

0.32

0.43

0.63

introduced a variation of nearly 13 per cent. in the area of oil exposed. In addition there must be variations in the thickness of the glass bottoms and walls.

Allen⁴ is most indefinite in prescribing the conditions under which the evaporation test should be made. "A known weight should be placed in a watch glass, wide beaker or flat porcelain dish," and then heated. Again, "spindle oil should not lose more than 5 per cent. of its weight when absorbed by filter paper" and then heated.

According to Archbutt and Deeley,⁵ the volatility of an oil is commonly determined by heating 0.6 to 1.0 gram in a shallow dish or watch glass. Archbutt, however, pointed out that the amount of evaporation

In Table I are given the results obtained on heating 5 grams of an oil intended for use in automobile engine cylinders, in each of the shorter tubes and also in the pair of longer tubes 2 cm. in diameter. This oil is designated as "A."

Throughout this paper the time of heating is counted from the moment the flame under the bath was lighted until the tubes were removed.

It was thought advisable to repeat this series of determinations under exactly the same conditions. The results are given in Table II.

From the results given in these two tables it is evident that the amount of evaporation, though small in any case, is greater the larger the tube used. The figures showing the losses during the first 3 hours probably largely represent loss of moisture and a little volatile oil. During the next two periods of heating the differences between tubes of successively greater

¹ Lunge, *Chem.-Techn. Untersuchungsmeth.*, 5te. Aufl., Bd. III, p. 50.

² *Z. angew. Chem.*, **18**, 726-34 (1905).

³ *Ibid.*, **23**, 99-103 (1910).

⁴ *Coml. Org. Anal.*, **2**, ed. 2, II, pp. 128 and 136.

⁵ "Lubrication and Lubricants," pp. 191-195.

diameter stand out more clearly. The influence of the depth of the tube is also shown by the results obtained with tubes A and B (3 cm. deep) as compared with tubes C and D (5 cm. deep), all of which are of the same diameter.

A sample of transformer oil (oil "B") was found to show much greater losses on heating, besides bringing out more clearly the increase in the amount evaporated as the area of the oil surface increased. The results are given in the following table:

TABLE III—EVAPORATION OF OIL "B" AT 110°

Weight taken, 5.00 grams; depth of tubes, 3 cm.

TUBE	A	B	E	F	G	H	I	J
Diam. of tube, cm.....	2	2	3	3	4	4	5	5
Loss in 3 hrs., mg.....	15.5	19.5	25.7	29.1	66.1	64.5	126.4	112.6
Loss, per cent.....	0.31	0.39	0.51	0.58	1.32	1.29	2.53	2.25
Loss in 3 hrs. more, mg.....	18.6	15.4	26.0	37.8	63.9	70.0	128.2	117.3
Loss, per cent.....	0.37	0.31	0.52	0.76	1.28	1.40	2.56	2.35
Loss in 3 hrs. more, mg.....	18.2	16.3	48.4	42.4	88.6	84.0	119.7	130.0
Loss, per cent.....	0.36	0.33	0.97	0.85	1.77	1.68	2.39	2.60
Loss in 3 hrs. more, mg.....	18.7	20.6	38.7	42.1	75.2	74.8	113.8	127.4
Loss, per cent.....	0.37	0.41	0.77	0.84	1.50	1.50	2.28	2.55
Total loss, mg.....	71.0	71.8	138.8	151.4	293.8	293.3	488.1	487.3
Total loss, per cent.....	1.40	1.44	2.78	3.03	5.88	5.87	9.76	9.75

Tubes C and D (5 cm. deep) were heated at the same time as the shorter ones, and gave such low results that tubes 5 cm. deep of each of the larger sizes were made. In Table IV are given the results of two successive runs using these deeper tubes, and including the results obtained when C and D were heated with the shorter tubes.

TABLE IV—EVAPORATION OF OIL "B" AT 110°

Weight taken, 5.00 grams; depth of tubes, 5 cm.

TUBE	C	C	C	D	D	D	E'	E'	G'	G'	I'	I'
Diam., cm.....	2	2	2	2	2	2	3	3	4	4	5	5
Loss in 3 hrs., mg.....	3.0	7.1	9.0	2.6	6.6	8.6	15.0	19.7	62.9	74.4	124.8	152.9
Loss, per cent.....	0.06	0.14	0.18	0.05	0.13	0.17	0.30	0.39	1.26	1.49	2.50	3.06
Loss in 3 hrs. more, mg.....	2.4	5.6	6.2	1.9	5.3	6.6	12.4	18.7	56.8	71.6	126.8	137.3
Loss, per cent.....	0.05	0.11	0.12	0.04	0.11	0.13	0.25	0.37	1.14	1.43	2.54	2.75
Loss in 3 hrs. more, mg.....	3.3	6.0	5.2	3.2	5.9	5.7	16.8	19.1	67.9	67.0	129.4	124.9
Loss, per cent.....	0.07	0.12	0.10	0.06	0.12	0.11	0.34	0.38	1.36	1.34	2.59	2.50
Loss in 3 hrs. more, mg.....	5.3	6.9	4.6	4.5	6.9	4.6	20.6	14.6	81.8	38.9	113.5	87.5
Loss, per cent.....	0.11	0.14	0.09	0.09	0.14	0.09	0.41	0.29	1.64	0.78	2.27	1.75
Total loss, mg.....	14.0	25.6	25.0	12.2	24.7	25.5	64.8	72.1	269.4	251.9	494.5	502.6
Total loss, per cent.....	0.28	0.51	0.50	0.24	0.49	0.51	1.30	1.44	5.39	5.04	9.89	10.05

The results, while not as concordant as one could wish, show clearly, when compared with those in Table III, that with increasing depth of tube there is a lower rate of evaporation, except for the tubes of the greatest diameter. If the lower rate of evaporation in the deeper tubes is due to condensation on the upper part of the walls or to a hindering of the convection currents carrying away oil vapors, we should expect the effect to be least in the larger tubes, because a smaller proportion of the vapors comes in contact with the walls and there is more space for the free circulation of convection currents flowing in opposite directions. By the end of the third or fourth heating there were small amounts of oil around the outside of the mouths of the tubes, but no difference in this respect was noticed between the tubes of less or greater diameter, so that it would seem to be due to the ordinary "crawling" of the oil. From this, and from the excellent heat conductivity of brass, it seems that the hindering of the convection currents plays the principal part. The only practical way to avoid this effect is to have the oil vessels sufficiently broad and shallow.

As mentioned above, there was some evidence obtained months ago, tending to show that when quite different weights of the same oil are heated in vessels of the same size the losses are about the same when expressed in milligrams. To test this further, a series of determinations was made in the brass tubes 3 cm. in depth, using 1.0 gram of oil instead of 5.0 grams, as in the experiments described above. The two deeper tubes C and D were also used. The results are in Table VI.

The percentage losses are very much larger than when there was 5.0 grams of oil in each tube. The actual losses in milligrams, or what amounts to the same thing, the percentage losses calculated on the basis of 5.0 grams of oil, may be compared with the figures in Table III and with tubes C and D in Table IV.

As might have been predicted, the losses in the tubes

2 cm. in diameter (A to D) are less with one than with 5 grams of oil, on account of the relatively much longer air space in the tubes above the oil. A and B (Table V) when containing 1.0 gram have, however, about the same air space as C and D (Table IV) when holding 5.0 grams, and we find the losses in milligrams, roughly, the same.

With the tubes 3 cm. in diameter, E, F, and E', the losses are fairly comparable, showing the lessening influence of the air space in the tubes. With the tubes 4 cm. in diameter, G, H, and G', and still more clearly with the 5 cm. tubes, I, J, and I' (Tables III and V), we can see that the single gram of oil taken is approaching its limit of volatility at 110°, the total loss being naturally less than when 5.0 grams of oil were used. The losses in milligrams for the first six hours' heating for each size of tube above 2 cm. diameter are about the same, respectively, whether 1.0 or 5.0 grams of oil were taken (Tables III and V).

A series of determinations was made using Gill's method, described above. The eight drops of oil used each time did not weigh "about 0.2 gram," but

TABLE V—EVAPORATION OF OIL "B" AT 110°

TUBE	Weight taken, 1.00 gram									
	A	B	C	D	E	F	G	H	I	J
Diam. and depth, cm.....	2 x 3	2 x 3	2 x 5	2 x 5	3 x 3	3 x 3	4 x 3	4 x 3	5 x 3	5 x 3
Loss in 3 hrs., mg.....	7.0	8.7	3.1	3.4	26.6	35.1	79.0	80.5	121.4	156.4
Loss, per cent.....	0.70	0.87	0.31	0.34	2.66	3.51	7.90	8.05	12.14	15.64
Loss in 3 hrs. more, mg.....	8.5	7.6	3.0	2.8	39.6	31.9	67.8	68.4	105.2	85.4
Loss, per cent.....	0.85	0.76	0.30	0.28	3.96	3.19	6.78	6.84	10.52	8.54
Loss in 3 hrs. more, mg.....	7.0	7.4	3.4	3.1	31.2	34.5	58.8	55.5	70.7	74.2
Loss, per cent.....	0.70	0.74	0.34	0.31	3.12	3.45	5.88	5.55	7.07	7.42
Loss in 3 hrs. more, mg.....	5.4	7.8	3.1	3.0	22.9	28.8	54.1	40.6	55.6	47.0
Loss, per cent.....	0.54	0.78	0.31	0.30	2.29	2.88	5.41	4.06	5.56	4.70
Total loss, mg.....	27.9	31.5	12.6	12.3	120.3	130.3	259.7	245.0	352.9	363.0
Total loss, per cent.....	2.79	3.15	1.26	1.23	12.03	13.03	25.97	24.50	35.29	36.30
Averages, per cent.....	2.97			1.25	12.53		25.24		35.79	
Averages on basis of 5 grams oil, per cent.....	0.59			0.25	2.51		5.05		7.16	

the amount was sufficient to thoroughly saturate the ring of filter paper. The more volatile oil "B" was first heated. The results follow:

TABLE VI—EVAPORATION OF OIL "B" AT 110°

Gill's Method						
Weight of oil, gram.	0.1441	0.1490	0.1401	0.1436	0.1506	0.1409
Loss in 3 hours, mg..	45.6	55.3	44.8	49.4	46.2	43.1
Loss, per cent.....	31.64	37.11	31.98	34.40	30.68	30.59

Four determinations were also made on oil "A," together with two more on oil "B," for comparison.

TABLE VII—EVAPORATION OF OILS "A" AND "B" AT 110°

OIL	Gill's Method					
	A	A	A	B	B	B
Weight of oil, gram....	0.1431	0.1327	0.1407	0.1416	0.1407	0.1464
Loss in 3 hrs., mg.....	2.9	0.9	2.1	2.7	45.0	49.1
Loss, per cent.....	2.03	0.68	1.49	1.91	31.98	33.54
Loss in 3 hours more, mg.....	1.5	3.1	1.8	1.9	19.1	20.7
Loss, per cent.....	1.05	2.34	1.28	1.34	13.58	14.14
Total loss, mg.....	4.4	4.0	3.9	4.6	64.1	69.8
Total loss, per cent.....	3.08	3.01	2.77	3.25	45.56	47.68

A final series of determinations was made with oil "B," using filter papers $1\frac{5}{8}$ inches in diameter, (a)

TABLE VIII—EVAPORATION OF OIL "B" AT 110°

PAPERS	Gill's Method with Modifications								
	No holes			$\frac{5}{8}$ -inch holes			$2\frac{1}{2}$ inch holes		
Weight taken, gram.....	0.1124	0.1104	0.1063	0.1142	0.1061	0.1023	0.1034	0.1021	0.1063
Loss in 3 hrs., mg.....	36.1	36.3	36.9	44.5	47.6	40.9	37.1	41.2	34.7
Loss, per cent.....	32.12	32.88	34.71	38.97	44.86	39.98	35.88	40.35	32.64
Loss in 3 hrs. more, mg.....	13.1	10.4	11.6	9.7	7.8	8.5	11.4	10.6	9.9
Loss, per cent.....	11.65	9.42	10.91	8.49	7.35	8.31	11.03	10.38	9.31
Loss in 3 hrs. more, mg.....	12.2	14.2	10.0	9.8	10.9	10.4	9.2	9.8	9.7
Loss, per cent.....	10.85	12.86	9.41	8.58	10.27	10.17	8.90	9.60	9.13
Total loss, mg.....	61.4	60.9	58.5	64.0	66.3	59.8	57.7	61.6	54.3
Total loss, per cent.....	54.62	55.16	55.03	56.04	62.49	58.46	55.81	60.33	51.08

without holes cut in them, (b) with $\frac{5}{8}$ -inch holes, and (c) with $2\frac{1}{2}$ -inch holes, respectively. Since six drops of oil saturated the last papers, this amount was used throughout.

With an oil of comparatively high volatility it appears that the results obtained by heating on filter paper are not to be compared, as far as their concordance is concerned, with those obtained by heating in brass tubes. The total losses, in milligrams, observed with a less volatile oil ("A" in Table VII) are much more concordant, but when calculated as percentages they may show wide variations unless care is taken to weigh out always exactly the same quantity.

Although in the above experiments the oil was always heated to 110°, it is believed that the differences would be of the same order at lower or higher tempera-

tures. The only object in heating the oil is to hasten an operation that must be taking place at ordinary temperatures, though much more slowly. In this connection may be given the results of some experiments made on a typewriter oil many months ago. It was this, indeed, which first showed clearly the need of very exact duplication of all of the conditions.

Portions of the oil were heated in 50 cc. Jena beakers and in ordinary weighing bottles of smaller diameter than the beakers. The dimensions were not recorded.

TABLE IX—EVAPORATION OF TYPEWRITER OIL

VESSEL	Beaker		Weighing bottle	
	0.6027	0.8666	0.6786	0.8610
Weight of oil, gram.....				
Loss in 5 hrs. at 55°, mg....	6.5	7.3	4.0	5.3
Loss, per cent.....	10.78	8.42	5.90	6.16
Loss in 4 hrs. more at 55°, mg	9.4	9.8	3.3	3.7
Loss, per cent.....	15.60	11.31	4.86	4.30
Total loss, mg.....	15.9	17.1	7.3	9.0
Total loss, per cent.....	26.38	19.73	10.76	10.45

These figures pointed so clearly toward the need of having equal surface areas of oil exposed that two determinations were made, using 5.5 cm. filter papers in wide weighing bottles.

TABLE X—EVAPORATION OF TYPEWRITER OIL AT 55°

Weight of oil, gram.....	0.5835	0.6837
Loss in $3\frac{1}{2}$ hrs., mg.....	13.5	13.6
Loss, per cent.....	2.31	1.99
Loss in 3 hrs. more, mg.....	6.1	6.1
Loss, per cent.....	1.05	0.89
Total loss, mg.....	19.6	19.7
Total loss, per cent.....	3.36	2.88

Finally, samples of the oil were exposed at room temperature in wide weighing bottles covered with filter paper to exclude dust.

TABLE XI EVAPORATION OF TYPEWRITER OIL AT ROOM TEMPERATURE

Weight of oil, Feb. 21, gram.....	0.6066	0.7439
Loss by Mar. 1, mg....	0.8	0.8
Loss, per cent.....	0.13	0.11
Further loss by Apr. 3, mg.....	6.1	6.0
Loss, per cent.....	1.01	0.80
Total loss, mg.....	6.9	6.8
Total loss, per cent.....	1.14	0.91

It would seem as if sufficient evidence has been presented in this paper to show that, in order to obtain comparative results, the same weight of oil must always be heated in vessels of the same size, so that the oil surface shall always be the same in area and the convection effects be alike. Brass vessels are preferable to those of glass, because they can be made with their walls and bottoms of the same thickness, thus insuring more uniform heating. A convenient size is 5 cm. in internal diameter with sides 3 cm. high. Tubing of this size with a wall thickness of 0.75 mm. can be bought. The bottoms may be made of sheet brass not more than 0.5 mm. thick. It is best to use silver solder, so that the heating need not be limited to the lower temperatures. A vessel of the size indicated weighs somewhat less than 42 grams.

A convenient weight of oil is 5.0 grams. To avoid smearing oil on the walls of the tubes the writer used a small pipette with a 2 cm. stem below the bulb. The final adjustment of the weight was made by just touching an oily or a dry stirring rod to the surface of the oil. It is comparatively easy to weigh out the oil within 0.5 mg. of the amount desired, though a much larger variation would be of little consequence in calculating the percentage of evaporation.

In a neutral atmosphere there might have been somewhat greater losses, and possibly still greater differences between the losses with increasing diameter of tube, than the amounts given in the tables above. In the air there is more or less oxidation, partly involving loss of carbon dioxide and water, but mainly due to the formation of compounds containing carbon, hydrogen and oxygen, which are precipitated in part from the oil as a fine, brown sediment. The observed losses are really the sum of volatile oil, carbon dioxide and water lost, minus the oxygen taken up.

It would be interesting to repeat the work herein described, using an atmosphere of carbon dioxide, nitrogen or steam instead of air, but the results would be of less general application.

BUREAU OF STANDARDS
WASHINGTON, D. C.

PRELIMINARY NOTE ON A NEW METHOD FOR THE DIRECT DETERMINATION OF RUBBER¹

By L. G. WESSON

The chief difficulty that has stood in the way of the direct determination of rubber has been the uncertain composition of the derivatives, such as the tetrabromide and nitro compounds, used in the methods proposed up to date. This has suggested a method which avoids this source of error by forming a derivative, the nitrosite, whose composition is immaterial so long as it contains all the carbon which belonged to the rubber of the sample under analysis. On analyzing this derivative for carbon, we are then enabled to calculate how much rubber the derivative represents.

The procedure, in brief, consists in allowing the acetone-extracted sample to dissolve or swell up in

carbon tetrachloride, after which nitrous gases, evolved by dropping HNO_3 on As_2O_3 , form the nitrosite of rubber by passing through the solution to saturation. After standing, the now soluble nitrosite is dissolved in acetone, from which it is obtained in a form ready for combustion by a method of precipitation or evaporation. The details of both of these methods are being studied to eliminate known sources of error, and to further simplify the manipulation.

The tediousness of the latter has been considerably relieved by the development of a durable electric organic combustion furnace adapted for this work. It consists of a tube of Jena glass 60 cm. long and of $2\frac{1}{2}$ cm. bore, containing a coil of electrically heated platinum wire, and a boat of lead peroxide and minium heated by an external coil of nichrome wire. Two heavy copper wires, coated with iridium and pushed through the one-holed rubber stopper at the forward end of the tube, solve, in a convenient manner, the problem of making an external contact for the useful, directly heated catalyzer coil. The leads for the coil simply rest on the hooked ends of these wires, thus permitting an easy removal and replacement of the stopper, the coil, or the lead peroxide boat which rests between the coil and the stopper. It is thought that, with a few modifications, this form of furnace is adapted for general organic combustions, and it will be tested soon with that end in view.

The use of the lead peroxide boat which absorbs the sulfur of the nitrosite as lead sulfate, should give a means for the estimation of the sulfur of vulcanization, if, as Alexander emphatically asserts,² the sulfur combined with the rubber is carried quantitatively into its nitrosite.

The following figures have been obtained by the use of either the precipitation or evaporation methods:

A washed and dried fine para, precipitated once from chloroform, dried to constant weight in hydrogen at 92°, and analyzed as 99.1 per cent. carbon plus hydrogen, gave 99.5, 98.7, 97.8, 98.0, 97.1 and 96.6 per cent. $\text{C}_{10}\text{H}_{16}$.

A washed and dried fine para gave 95.7, 94.7, 94.8, 95.2, and 95.5 per cent. $\text{C}_{10}\text{H}_{16}$.

A rubber compound containing litharge, whiting, barytes, zinc oxide, sulfur, and 48 per cent. para, or 45.4 per cent. rubber, gave 45.3, 46.4, 48.7, 47.2, and 45.6 per cent. $\text{C}_{10}\text{H}_{16}$.

Another containing the same ingredients with the addition of paraffin, with 28.6 per cent. fine para or 27.8 per cent. rubber, gave 27.5, 27.4, 27.7, 26.7, 27.1, and 26.9 per cent. $\text{C}_{10}\text{H}_{16}$.

These results, however, represent only those that have been obtained under the best conditions, and are not subject to the numerous sources of error that have continually appeared. They seem to be of sufficient value to justify putting on record at this time. Further work should give a greater reliability and accuracy, in which case full details of the method and apparatus will be published.

BUREAU OF STANDARDS
WASHINGTON

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913. Published by permission of the Director of the Bureau of Standards.

² *Ber.*, 40, 1077; *Z. angew. Chem.*, 20, 1364; 24, 687.

RAPID DETERMINATION OF SULFUR IN PYRITES CINDER

By A. B. CONNER

Received December 9, 1912

In THIS JOURNAL,¹ Mr. C. C. Nitchie described a rapid method for the determination of sulfur in roasted blende which is carried out by roasting the sample in a boat in an electric combustion furnace, in a current of pure dry air, absorbing the acid gases in standard sodium hydrate solution and titrating the residual alkali with equivalent standard acid.

Nitchie suggested that the method could be applied to the determination of sulfur in pyrites cinder and immediate trial was given this suggestion in the writer's laboratory, with entire success; it has been in constant use daily for the past ten months with results that are all that could be desired.

As the article referred to is very complete in its directions, it will only be necessary to mention in outline such modifications or changes as have been found satisfactory during the period of its use. Instead of the furnace mentioned, a Hoskins tube furnace such as is in common use for the direct combustion of carbon in iron and steel was at hand and proved well suited for the work. This furnace takes a fused silica tube three-quarters of an inch by twenty-four inches or even one of larger bore if desired. The three-quarter inch size seems best for this work and is made quite rigid in the furnace by a turn or two of one strand of three-eighths inch pure asbestos rope packing gently packed around the tube in each opening of the furnace. The furnace covers one foot of the tube leaving six inches of each end projecting; the ends do not need to be water-cooled.

The asbestos shield described for the outlet stopper proved sufficient protection and the gases only just warm the absorption bulb, unless the aspiration is too rapid. An ordinary water filter pump or aspirator is used for drawing the gases through the train. A Muencke's glass filter pump, operated by compressed air instead of water, with a needle valve on the air supply, gives finer control and is preferred by the writer. The pump is connected to the six-bulb Murray potash bulb by rubber tubing and a further control of the aspiration is obtained by the use of a screw pinch-cock on this tubing.

The Murray bulb tubes are furnished by E. H. Sargent & Co., and those with an opening for a No. 3 rubber stopper are most easily handled. It is necessary to specify the opening since they are also made for No. 0 stoppers. A ten-bulb Meyer tube of similar type may be used, but is a trifle more cumbersome.

The air is freed from CO₂ and dried by bubbling through a bottle containing about 200 cc. of 1 : 1 KOH and then through a calcium chloride tower filled with quarter-inch granular CaCl₂ and is led to the combustion tube by a foot or more of rubber tubing connected by glass to a rubber stopper for closing the entrance end. This stopper need not be protected.

When first started, the furnace² should be heated

up gradually by cutting out resistance from the rheostat and the silica tube should be bedded with a layer of 20-mesh silica sand which has been digested for some hours in strong HCl, washed, and dried in an oven, or with 20-mesh grained alundum such as is furnished by the Norton Co. for carbon combustions. This bedding should be done before the first heating up and before the introduction of the couple, if this is put into the tube. It is easily accomplished by filling a boat with the silica or alundum and introducing it into the tube after this is in the furnace in position for working. The boat is pushed into the far side of the furnace zone of the tube, slightly inclined to spill a portion of the sand and gradually withdrawn, at the same time tipping the boat until, as it reaches the near end of the tube, it has been completely overturned and the sand has been distributed in an even layer along the bottom of the tube and back to the position occupied by the entrance rubber stopper. This serves as a medium on which the boat slides easily and lessens the likelihood of breakage of the tube. No breakage, however, has occurred with this equipment.

A one-gram sample is put into a No. 5733 alundum boat which has been bedded with a layer of about one-sixteenth inch of silica sand, washed and dried as above mentioned and previously ignited in the furnace. If the sample rests on unignited sand the decrepitation of some of the grains of sand will throw the cinder out into the tube, which will be attacked by the iron oxide. Should this occur or should a sample be spilled in the tube, the furnace should be shut off, allowed to cool, and the tube emptied, brushed out with a burette brush, replaced and "rebedded."

A convenient way of handling the work is to switch on the furnace the first thing in the morning. About an hour and a half to two hours is required for the furnace to come to maximum heat with the rheostat set for 1000° C. and in the meantime the sample may be prepared and the bulb filled. While the article by Mr. Nitchie states that roasted blende samples need be ground only fine enough to secure an average sample in one-gram, 60 to 80 mesh seems necessary with pyrites cinder and 100 mesh or even finer material requires apparently only two or three minutes longer for complete oxidation; so that if the sample has been prepared in a disc grinder and this has been set a little closer than was intended, it is only necessary to allow about five minutes' longer aspiration.

Twenty-five cc. of standard alkali (1 cc. = 5 mg. S) are run into the bulb (preferably from an automatic pipette) and diluted as described in the paper cited, so that on aspiration the liquid extends into the fifth bulb. The necessary amount can be ascertained by trial by inclining the tube so that the liquid runs into

with the necessary leads and ammeter which are specially designed for continuous use with the furnace. This is quite desirable if the voltage of the electric supply is not constant since the life of the furnace winding is shortened when the temperature is carried higher than necessary. If the voltage is constant the temperature can be taken with the regular thermo-couple in the combustion tube at the time the furnace is first put in use and the setting of the rheostat made thereby. From two weeks to a month later the setting of the rheostat should be checked in the same way, and from time to time thereafter as the winding changes slightly in its resistance with use.

¹ THIS JOURNAL, 4, 30.

² The temperature used is 1000° C. and is regulated by a rheostat furnished with the furnace. The setting of the rheostat is determined by a thermo-couple. The makers of the furnace can also supply together

the bulbs from the large bulb. Twenty-five cc. are used instead of the seven to ten mentioned, since this gives a larger excess alkali and a trifle greater accuracy. The bulb is placed in position, the aspiration started and regulated to twenty-five bubbles in ten seconds. The stopper is removed and the boat pushed into the center of the tube by the rod which is provided with a distance guard of fine wire. The stopper is replaced and the aspiration continued for ten or twelve minutes for moderately fine samples, or fifteen minutes for those of 100-mesh grain or over. Almost immediately on placing the boat in the furnace the sulfur gases are seen to commence passing over and they continue to be visible for several minutes. In most cases the fume seems to pass entirely through the set of bulbs. Actually a trace of SO_2 does pass them, but it is negligible. If the ore contains even a few tenths of one per cent. of zinc this increases the white cloud and may lead to the belief that SO_2 is being lost. The results below show that for practical purposes the loss need not be given further thought.

At the end of the specified time the furnace is shut off if no more samples are to be tested, the bulb is disconnected and its contents are washed into a tall 500 cc. beaker and titrated, using phenolphthalein and equivalent standard acid, the formula for calculation being:

$$\frac{\text{cc. alkali} - \text{cc. acid}}{2} = \text{per cent available S in cinder.}$$

It is customary, at our works, to test one average sample from the burners daily or, if more than one kind of pyrites is being burned, a sample of the cinder from each. This, in connection with an exact figure for the available sulfur in the pyrites and the chamber and tank "dips," daily, gives a reliable check on the production of the plant. The sample is obtained by taking a part shovelful from each barrow or truck of cinder as it is wheeled out, and placing in a box. Each morning the accumulation is mixed and quartered by the head furnaceman and a pailful sent to the laboratory, where it is ground in a Sturtevant disc pulverizer after being crushed in a roll jaw crusher of like make. Fifteen to twenty minutes is required to prepare the sample for analysis.

The following table shows the comparison between the regular (Br-KBr-HNO_3) gravimetric method for residual available sulfur in cinder and the results by this combustion method. The figures include results on a number of foreign and domestic ores and are well scattered over the period that the method has been in use.

The majority of the figures given are selected from those showing sulfur considerably above the average, as these were the ones most frequently checked, and they show the closeness of the two methods.

The following method and check methods mentioned are intended to give available residual sulfur in cinder but it must be borne in mind that the meaning of this term must take into consideration the available sulfur in the pyrites and the method of its determination. The wet or Lunge method is the one most commonly

used and it is with this in mind that we may discuss availability.

RAPID DETERMINATION OF SULFUR IN PYRITES CINDER

Per cent S. Regular method	Per cent S. Combustion method
0.77	0.75
1.49	1.60
1.96	2.00
2.45	2.43
2.46	2.30
3.00	3.05
3.32	3.45
3.36	3.43
3.43	3.65
3.47	3.55
3.66	3.53
4.10	4.13
4.14	4.15
4.23	4.15
5.21	5.30
6.29	6.15
6.68	6.50

RESULTS OF TOO RAPID ASPIRATION	
Per cent S. Comb. meth.	Per cent S. Comb. meth.
25 bubbles in 10 sec.	Nearly twice as fast
2.50	1.80
4.13	3.85
5.15	4.70

The original available sulfur is that occurring as sulfides, oxidizable by combustion with air, and any sulfates soluble in the dilute hydrochloric acid used in getting the baked residue into solution in the original analysis of the pyrites. Any sulfur compounds, such as BaSO_4 , or equivalent barium compounds (carbonate, etc.), do not enter into the question of availability, either in the pyrites or in the cinder, and hence must not be estimated in the cinder. This precludes the use of a fusion method, either peroxide or carbonate, where there is any possibility of these compounds occurring in the pyrites. They are nearly always present to a greater or less extent, hence fusion methods are practically out of the question except for total sulfur, which is not what is wanted in the usual cinder test.

In burning pyrites some sulfur is oxidized and combines with the iron compounds to form sulfates. These, of course, constitute available sulfur in the original pyrites and must be estimated along with the unoxidized sulfide, etc. A simple extraction with cold water will prove their presence when the extract is treated with barium chloride. The writer has always found them present in all the kinds of cinder ever examined, and it is safe to conclude that they are always present. With many kinds of pyrites the major portion of the available sulfur left in the cinder is in the form of soluble sulfates. It also depends quite largely on the conditions during burning. With one Spanish ore as much as 80 per cent of the remaining available sulfur has been found in the form of soluble sulfates. Sulfites are also frequently present and must be included.

It is certain from complete analyses of quite a number of varieties of Spanish and domestic ores that lime is an almost constant constituent, but in nearly all cases only a few tenths of a per cent are found, seldom exceeding 0.5 per cent and more frequently only 0.2-0.3 per cent.

As recently pointed out by A. M. Smoot,¹ this lime as sulfate is not insoluble in the course of the regular wet assay of pyrites and its sulfur is estimated as available sulfur. This being so it should rightly be included as such in the cinder, but from recently published data concerning the decomposition temperature of sulfates it would seem as though the combustion method would not include this. The temperature given for the decomposition of CaSO_4 is $1200^\circ \text{C}.$ ²

Mr. Nitchie finds that CaSO_4 is not decomposed in his method of analyzing roasted zinc blendes. If so, the sulfur equivalent to the lime should remain in the furnace with the ferric oxide obtained by roasting pyrites cinder. My check analyses by gravimetric means indicate that if the lime is combined with sulfur in the cinder, the combination is broken during the test and the sulfur evolved as gas. It is probable that the ferric oxide plays some part in this reaction. If, however, the lime retained its equivalent of sulfur it would, as seen above, amount with most kinds of pyrites to only one or two-tenths of one per cent.

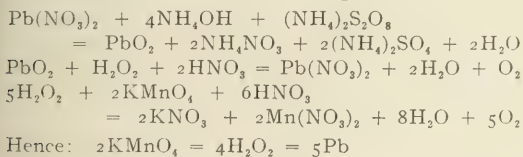
Two grades of Spanish pyrites with which the writer is quite familiar contain several per cent of zinc and a number of others smaller amounts. By the water test above referred it is easy to determine that some of the soluble sulfate is present in combination with zinc. What Mr. Nitchie says about zinc sulfate in roasted blende applies to pyrites containing zinc, but the reactions may include the action of iron sulfide and oxide on zinc sulfate for the results indicate a complete decomposition of this last salt.

DETROIT, MICH.

A NEW TECHNICAL METHOD OF SPELTER ANALYSIS³

By ERIC JOHN ERICSON

At the Sixth International Congress in Rome, 1906, chemists were invited to publish their methods of spelter analysis for comparison and possible unification. Hence I now present a scheme, involving the application of an original method for lead, which, at the same time, effects a separation from cadmium. The fundamental reactions were described in the *Journal of the American Chemical Society*, September, 1904, and subsequently in the *Engineering and Mining Journal*, July 25, 1908, and May 22, 1909, giving its application to ores. It is based on the following reactions:



Since the theoretical factor $\frac{5\text{Pb}}{10\text{Fe}} = 1.851$ gives too

low results, the empirical factor 1.92 was chosen—giving results agreeing exactly with the standard gravimetric method—whenever a preliminary separation of lead is not necessary, and 1.95 for ores where such

separation is essential. The reason for requiring a higher factor than the theoretical is believed to be due to the lead peroxide carrying one-half molecule of water.

Solution of the spelter sample is effected by dilute hydrochloric acid according to Oswald Gunther¹ or dilute sulfuric according to Eliot and Storer, until nearly all zinc is dissolved. This procedure makes it possible to operate on a large sample and each 0.1 cc. of potassium permanganate (0.568 gram to the liter) equals 0.001 per cent lead, when 19.2 grams spelter is taken. The insoluble lead, cadmium and some zinc is filtered off, washed, dissolved in nitric acid, diluted, ammonia and ammonium persulfate added to peroxidize the lead. After filtering, the cadmium may be precipitated in the filtrate by hydrogen sulfide.

The substitution of trichloroacetic acid, according to Fox,² for any one of the mineral acids usually employed in separating cadmium and zinc, has been found advantageous, since it is not dissociated to the same extent as hydrochloric or sulfuric acids, and even rather concentrated solutions do not prevent the complete precipitation of cadmium. In the case of mineral acids the strength must be kept within narrow limits, as is well known. A slight excess prevents the complete precipitation of cadmium, while insufficient acid causes zinc also to be precipitated, making several reprecipitations necessary. By means of trichloroacetic acid usually only one re-precipitation is called for, unless it is accompanied by more zinc than was aimed at originally in dissolving.

ANALYTICAL METHOD

Weigh out 19.2 grams of the spelter and place in No. 3 beaker. Add 200 cc. ordinary water and 43 cc. concentrated hydrochloric acid (1.2 sp. gr.), or 100 cc. water and 50 cc. dilute sulfuric acid (1:3); allow to stand over night whenever cadmium is to be determined; if lead alone is wanted a few hours' time will do. Filter off metallic, consisting chiefly of lead, cadmium and some undissolved zinc, and wash with hot water. Transfer whatever metallics are on the filter paper back into the beaker by means of a jet of water. This can be accomplished without loss if done at once before the paper gets dry. Now add 10 cc. concentrated nitric acid and boil until brown fumes cease to come off. Filter and wash if traces of tin or antimony are indicated, which is very seldom the case. If filtered and washed the volume will probably be large enough; if not filtered, add 100 cc. distilled water, 30 cc. concentrated ammonia and 5-10 grams ammonium persulfate, depending on size of precipitate. Should lead be unusually high, say over 1.00 per cent, it is best to add half of the persulfate before adding the ammonia. Boil five minutes and allow ten more for the precipitate to settle. Then filter while still warm through double 11 or 12.5 cm. No. 1 F filters. Wash four times with a hot 10 per cent ammonia solution and five times with hot

¹ Eng. Min. J., 94, 412.

² Met. and Chem. Eng., 10, 172.

³ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

¹ Bericht der Internationalen Analysen Kommission an der VI Internationalen Kongress für Angewandte Chemie in Rom, 1906, p. 51.

² Jour. Chem. Soc., London, 1907, p. 964.

water. Transfer filter with precipitate back into same beaker in which precipitation was made. Add 25 cc. hydrogen peroxide solution (10-50 cc. hydrogen peroxide U. S. P. strength to the liter, plus 50 cc. concentrated nitric acid). Stir until dissolved, add 15 cc. nitric acid, (1.20 sp. gr.) plus 75-100 cc. distilled water and titrate the excess of the hydrogen peroxide by standard potassium permanganate of the strength indicated above. For instance, if 25 cc. H_2O_2 blank requires 80.0 cc. KMnO_4 and the sample 34.5 cc. then the lead equals $80.0 - 34.5 = 0.455$ per cent. If 25 cc. of the H_2O_2 solution should fail to dissolve the lead peroxide, add another 25 cc. and double the blank. The accompanying samples taken from practice, show that the new method checks exactly with the long chromate method:

	Ericson method	Gravimetric(a) as chromate
Refined spelter.....	0.052 per cent lead	0.055 per cent lead
Refined spelter.....	0.082	0.083
Refined spelter.....	0.043	0.044
Prime Western spelter.....	0.530	0.538
Prime Western spelter....	0.533	0.531
Special spelter.....	$\left\{ \begin{array}{l} 1.272 \\ 1.283 \end{array} \right\}$	1.279

(a) Filtz, *Praktische Leitfaden für Zinkhütten-laboratorien*, p. 27.

For spelter rather high in lead, it will be advisable to check the lead factor against a standard spelter, under identical conditions.

CADMIUM DETERMINATION

Boil the ammoniacal filtrate from lead until nearly neutral and a white precipitate appears, then take off hot plate and add 40 cc. dilute sulfuric acid (1 : 3) and boil about ten minutes. Add water to make the volume about 200 cc. and saturate with hydrogen sulfide gas, adding a little water occasionally. Allow the precipitate to settle, filter through double filters and wash a few times with water. Redissolve on the filter the cadmium sulfide contaminated with zinc sulfide, in as little warm dilute hydrochloric acid as possible and wash with warm water. If copper is present, the sulfide remains insoluble on the filter. It may be ignited and weighed as CuO or colorimetrically.

The filtrate containing the chlorides of cadmium and zinc is nearly neutralized with dilute ammonia and about 8 grams of trichloroacetic acid dissolved in water added, or enough to dissolve the CdS formed by neutralization. Add distilled water to about 200 cc. volume and reprecipitate Cd by H_2S . Allow to settle, filter and determine by any of the usual methods, preferably as sulfate or phosphate. Duplicate determinations usually agree within a few hundredths of 1 per cent.

Iron is determined in a separate sample by dissolving 10 grams in 75 cc. dilute sulfuric acid and allowing it to stand until practically all dissolved; a few drops of platinum chloride added to effect complete solution; then titrate with the same standard permanganate solution used for lead. Each 0.1 cc. KMnO_4 solution equals 0.001 per cent. iron on a 10-gram sample basis.

The method outlined above takes care of the usual constituents called for in spelter analysis, such as lead,

iron and cadmium. Zinc is taken by difference. Copper, tin and antimony are indicated and may also be determined, whenever present. The lead method is a marvel of accuracy and gives very concordant results. In making this claim, I am aware of recent criticism in regard to shortcomings of most analytical methods proposed. This one will be found, on investigation, to be a notable exception, and its daily use for several years has fully demonstrated its reliability.

EDGAR ZINC CO.
ST. LOUIS

FACTORY METHOD FOR THE DETERMINATION OF TOTAL FATTY ACIDS IN COTTON-SEED FOOTS¹

By F. N. SMALLEY

The method herein described is proposed for a rapid method for the determination of the total fatty acids in cotton-seed foots, or soap stock, and similar materials, by a determination of the iodine number of the same, and its conversion into terms of fatty acids by means of an appropriate factor.

Cottonseed oil soap stock is the sludge removed from crude oil in the process of refining with caustic soda, and consists of the soda soaps of the fatty acids of the oil, together with some neutral oil, coloring and albuminous matters which are characteristic of crude oil, caustic soda and water.

The most accurate method of the determination of the total fatty acids is the Official Method of the Interstate Cotton-seed Crushers Association, which consists in complete saponification of the fat by means of alcoholic soda, evaporation of the alcohol, solution of the soap in the hot water, decomposition of the soap with dilute mineral acids, melting of the liberated fatty acids, chilling to form a cake, filtering and washing free from mineral acid, extraction of the cake with warm petroleic ether, evaporation of the solvent and weighing of the residual fatty acids.

The method is so long that it is almost useless for factory control, and for that reason after trials of a number of various proposed methods, the iodine method was selected in the summer of 1905, as the best fitted to obtain the most accurate results in the shortest time. Since then it has been in continuous use in the refineries of the Southern Cotton Oil Company.

The method is carried out as follows: After the sample has been well mixed, weigh out accurately 0.5 gram on to a small square of fat-free paper. This is then introduced into a ground glass stoppered bottle with neck so arranged that the joint can be sealed with the potassium iodide solution. Five cc. of carbon tetrachloride and 20 cc. of Wijs' iodine solution are added. The bottle is stoppered and the contents gently shaken until the soap stock is in solution. Seal with potassium iodide solution and allow to stand for thirty minutes.

The determination of the iodine number is now carried out in the usual Wijs' method, and the resultant number is converted by division by 1.24 into per cent fatty acids.

The factor was arrived at by comparison of the

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

iodin number with the total fatty acids as determined by the official method as before outlined. Some one hundred and fifty samples were analyzed by both methods before the final selection of the factor was made.

The following table shows the closeness of the two methods.

Sample number	F. F. A. by official method	Iodine No.	F. F. A. by calculated for I No.
2171	43.39	53.53	43.17
72	40.70	50.90	41.05
75	47.35	58.68	47.32
76	46.70	57.64	46.48
77	49.34	60.71	48.96
78	47.13	58.16	46.90
79	46.51	57.13	46.07
81	48.48	58.88	47.48
84	51.52	61.19	47.31
87	49.30	61.0	49.20
88	46.67	47.34	38.18
90	47.45	58.66	47.31
91	49.31	61.48	49.58
92	47.03	58.16	46.90
94	49.29	61.19	49.35

The above represented one day's work, and the results are typical of all work done. The three samples 2181-84-88, which show the greatest difference, were several weeks old and fermentation was in an advanced stage.

The results showed that the conversion factor could not be depended on if the soap stock was more than a week old, but as the whole purpose was to obtain results as soon as possible after the refining was made, this was no serious objection.

The six years' use has proven that the method, as used, gave, on the whole, extremely satisfactory results, and it has only received minor modifications, consisting in using special strength of sodium thio-sulfate and iodine solution, so as to simplify the calculation.

SAVANNAH, GEORGIA

THE MODIFIED BABCOCK FOR FAT IN SWEETENED DAIRY PRODUCTS—ICE CREAM¹

By J. O. HALVERSON²

DIFFICULTIES IN TESTING SWEETENED DAIRY PRODUCTS BY THE BABCOCK TEST

The Babcock test is not applicable to sweetened dairy products on account of the charring action of the acid on the sugar. This causes a black charred mass to rise in the neck of the test bottle. Nor can the Adams-Soxhlet method be depended upon as the sugar particles enclose fat.³ Leach³ overcomes this by pipetting off this solution containing sugar after precipitating the proteids with the fat by Fehling's copper sulfate solution. He then centrifuges in the cold, washes twice with water. The chances for errors are in thrice pipetting off the sugar solutions. Errors are also increased three-fold by multiplying the final reading by three.

¹ Paper presented at the Annual meeting of the American Chemical Society, Milwaukee, March, 1913. A preliminary report was read at the Washington meeting of the A. O. A. C., September 17, 1912.

² Formerly Deputy Food and Drug Commissioner, Acting Analyst, Missouri Department of Food and Drug Inspection, Columbia, Mo. Patents dedicated to the public are pending on the novel features of the test bottle described in this article.

³ Leach, *J. Am. Chem. Soc.*, **1900**, p. 589.

Later, in 1900, Farrington¹ published a method of coagulating the proteids with small portions of 3 cc. of sulfuric acid, centrifuging at 1000 revolutions for six minutes with the tester heated to a temperature of 200° F. This gathered the proteids with the fat into a firm lump, so the sugar solution could be poured out the neck. Ten cc. of water are then added and the curd shaken up, 3 cc. of acid added and the process continued as above. After most of the sugar is removed, 10 cc. of water are added and continued as in the Babcock test.

These are the modified Babcock methods used to remove sugar from sweetened condensed milk. Where the per cent. of fat runs high, as in ice cream, these methods do not precipitate all the fat, part of which rises to the surface. Hence these methods are inapplicable.

GRAVIMETRIC AND VOLUMETRIC METHODS IN USE ON ICE CREAM

For ice cream gravimetric methods are used as the Roesse-Gottlieb Extraction Method² and Paul's Method,³ a combination of the Leach and the extraction method. The fat obtained is finally weighed in both these methods.

Of the volumetric methods, none remove the sugar entirely, but attempt to minimize its interference the most possible. Such a method is that of Holm.⁴ This consists of a mixture of equal parts of glacial acetic and hydrochloric acid on a nine-gram sample. This acid used is less liable to char the sugar.

Howard⁵ uses 10 cc. of Fehling's Copper Sulphate Solution, shakes and centrifuges 3 minutes to precipitate the proteids. First chloroform is added, which dissolves the fat. He then removes the supernatant liquor. The chloroform is then driven off by running in steam.

The elimination of sugar in sweetened dairy products would make the Babcock test available as a rapid, easy method for the determination of fat.

It was thought if the sugar could be drained off after all the curd was practically dissolved by the ordinary acid used in testing cream and after the fat was centrifuged to the top, the Babcock could still be used as a rapid volumetric method for determining fat in ice cream and other sweetened dairy products.

It was observed that in the Babcock method in testing ice cream, an appreciable interval of time elapses on adding sulfuric acid slowly before action on the sugar begins. This is the basis of the proposed Modified Babcock Method and the essential point in this method. The acid-sugar solution is readily drained off by using a modified cream test bottle, which consists in fusing a small glass stopcock (1 mm. bore) on the side of a modified 6-inch 30 per cent cream test bottle. To drain off the acid containing the sugar, after centrifuging, equal parts of water and acid are added up to near the neck. Two minutes more centrifuging drives the fat and undissolved curd

¹ *Wis. Exp. Sta. Annual Report*, **1900**, pp. 86-89.

² *Landwe. Vers.*, **40**, 1-27 (1892).

³ *Bur. Chem., Circ.*, **90**, p. 10.

⁴ *Ann. Report, State Food Com., Illinois*, **1906**, p. 80.

⁵ *J. Am. Chem. Soc.*, **1907**, 1622.

to the top and the sugar is then drawn off by tilting the test bottle carefully, it being held in the left hand.

The test bottle was later modified to a 6 1/2-inch 25 per cent cream bottle (see Fig. 1), especially adapted for testing ice cream. This test bottle consists of a small glass stopcock (1 mm. bore) fused on the lower part of the bottle at an angle and placed at 90° to the right of the graduated readings. The graduation up to 25 per cent is based on an 18-gram charge, of which the smallest division reads to a quarter per cent.

can be modified for this purpose is shown in *Circular 202*, Bureau of Animal Industry, U. S. Dept. of Agric., p. 3, Fig. 1, which would consist in a modified top by fusing on the graduated neck of an ice cream bottle and its length changed to about one-half that given, to hold a corresponding volume of 45 cc.

TO DETERMINE FAT IN FRESH MILK WITH 20 PER CENT

(1 : 5) CANE SUGAR ADDED

It was then attempted to test sweet milk for fat to which 20 per cent cane sugar had been added. This

is the same proportion used in making ice cream. A few drops of formaldehyde were added and the milk samples kept in the cooler. This was designated "B." The part of the same milk unsweetened was marked "A."

The details of the modified method used are as follows: A charge of 17.6 cc. is taken to which is added 7 to 10 cc. of ordinary acid in small 3 cc. portions with shaking with a slight pause after each. When the color of the mixture of milk and acid has been slowly built up to the color of coffee with cream in it (an amber-brown)¹ 2 to 3 cc. of cold water are added with shaking to check the action. Centrifuge 5 minutes. Add hot water to near the neck and whirl 2 minutes more. Then carefully drain off the acid-sugar solution and again add acid in small portions till a *coffee-black* color is obtained (8 to 10 cc. of acid is approximately required). Add hot water up to near the neck and whirl 2 minutes more. (No precipitate will be left if carefully done and it will be unnecessary to drain a second time.) Run the fat into the neck with hot water. Whirl one minute and read. The results are given in Table I.

Results from determinations 1B to 4B were slightly low while the results from determinations 5B to 8B were practically the same as in fresh milk. These fat columns were as clear as those attained in ordinary work with milk and cream except determinations 5B to 8B, inclusive, which

were each perfectly clean and clear in a set of four run at the same time.

Determinations 1B to 8B, inclusive, were read under standard conditions, that is, in a hot water bath at 56° C. (limits used 54°-62°) and also with glymol. This latter is a white mineral oil used for removing the meniscus.

¹ Indiana Agricultural Experiment Station, *Bull.* 145, p. 560.

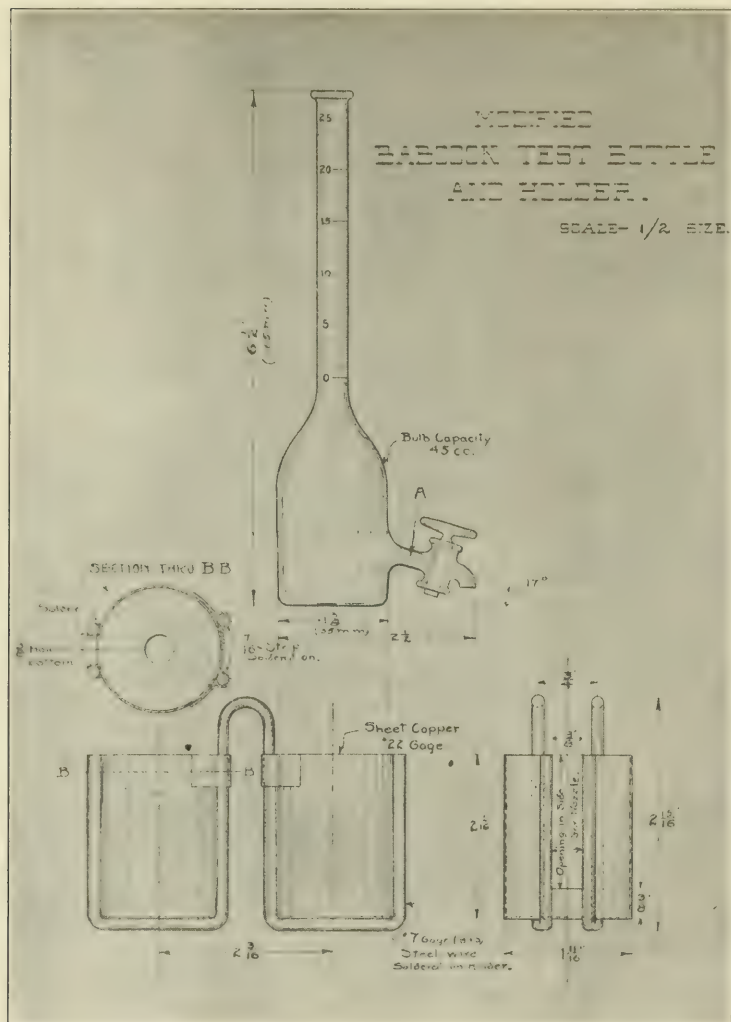


FIG. 1

Another modification that suggested itself for use in the large International centrifuges or in ordinary Babcock testers for use in food control laboratories is a modified pear-shaped separatory funnel with a 25 per cent graduated neck of an ice cream test bottle fused on the upper part and placed in trunnion collars or cups for centrifuging.

A special excellent form of separatory funnel which

TABLE I SWEET MILK PLUS 20 PER CENT CANE SUGAR ADDED

Determination number	Fat in "A" Unsweetened milk	Fat in "B" Sweetened milk
1.	4.30	3.9
2.	4.35	4.0
3.	4.40	4.0
4.	4.40	4.0
Average.	4.35	4.0
5.	4.20	4.4
6.	4.4	4.2
7.	4.4	4.3
8.	4.4	4.2
Average.	4.35	4.30

This indicated that by carefully dissolving out the curd and removing the sugar, good tests can be obtained.

COMPARISON OF PROPOSED METHOD WITH GLACIAL ACETIC ACID AND ROESE-GOTTLIEB METHODS

By using the same method and manipulation on ice cream as above with the exception that the action of the acid was checked with 5 cc. of cold water, comparisons were made of the proposed method with the glacial acetic acid and the Roese-Gottlieb extraction methods.

All the ice cream tested from the determinations 94 *a*, *b*, and *c*, to 99 *a*, *b*, *c*, and 100 *c*, were weighed out at the same time from a carefully mixed lot of ice cream. They were then kept until they could be run.

TABLE II COMPARISON OF PROPOSED MODIFIED BABCOCK AND GLACIAL ACETIC ACID METHOD WITH THE ROESE-GOTTLIEB METHOD

Det. No.	Modified Babcock method		Glacial acetic acid method		Roese-Gottlieb method	
	Charge Grams	Per cent. fat	Charge Grams	Per cent. fat	Charge Grams	Per cent. fat
		55° C.		58° C.		
94....	a—18.0	17.6	b—18.0	16.4	c—4.000	0.6985
95....	a—18.0	17.2	b—18.0	15.95	c—4.000	0.6892
96....	a—18.0	17.5	b—18.0	17.0	c—4.000	0.6947
		58° C.				
97....	a—18.0	17.55	b—18.0	19.5	c—4.000	0.6876
98....	a—18.0	17.25	b—18.0	18.35	c—4.000	0.6980
99....	a—18.0	17.00	b—18.0	17.4	c—4.000	0.7018
100....					c—4.000	0.6921
Average per cent.	17.35		17.433			17.436
Max. variation.	0.6		3.10			0.36

The results in Table II, by the proposed method, average 17.35 per cent., while that of the Gottlieb method averages slightly higher, 0.086 per cent. or 17.436. The glacial acetic acid method averages, by chance, apparently, the same as the Gottlieb, while the individual determinations vary considerably. The maximum variation for the Gottlieb method is 0.36 per cent., for the proposed method 0.6 per cent., for the glacial acetic acid method, a maximum of 3.10 per cent.

The fat column in 97 *c*, giving the highest reading by this method, had a heavy precipitate just below part of which may be mixed with the fat. The demarcation was not sharp and distinct. Determinations 98 *c* and 99 *c* contained also a precipitate beneath the fat column.

The ice cream used in Table II should run, according to calculations, from 17.5 to 17.75 per cent. fat, depending on the amount of sugar, which varied slightly.

These preliminary results on the accuracy and variation on the readings of the Modified Babcock agree

well. This was not true of the glacial acetic acid method, which was discontinued.

RESIDUAL FAT LOST IN THE PROPOSED TEST

It is known¹ that 0.2 to 0.3 per cent of fat is lost which never rises in the neck in the Babcock test of cream. To obtain the amount of fat thus lost, an 18-gram charge of 18 per cent ice cream in this proposed method was undertaken. The acid-sugar solutions drained off were extracted for fat with water-free ethyl ether. The results are given in Table III. These were obtained by extracting with 40 cc. of anhydrous ethyl ether, extracting a second time with 20 cc. A third extraction with 15 cc. gave practically no fat (from 1.9 to 3 mgs. with impurities) and so was discontinued. The ether was slowly distilled off from a small weighed Erlenmeyer flask on a water bath, dried in a steam oven and weighed to constant weight. The fat was then dissolved out of the flask with several portions of petroleum ether boiling below 60° C. The flask dried and the residue weighed to constant weight, which consisted of a few milligrams of dark, charred or decomposed sugar products.

TABLE III—RESIDUAL FAT LOST IN DRAINED-OFF PORTION ON 18-GRAM CHARGE IN 18 DETERMINATIONS

Determination number	Fat loss in grams	Fat loss in per cent.
88	0.0271	0.165
89	0.0185	0.103
90	0.0203	0.113
68	0.0464	0.257
69	0.0518	0.287
70	0.0477	0.265
82	0.0403	0.224
83	0.0930	0.516
84	0.0590	0.328
85	0.0440	0.244
86	0.0357	0.198
87	0.0598	0.332
1	0.0552	0.307
2	0.0526	0.292
5	0.0323	0.229
6	0.0495	0.275
7	0.0431	0.239
8	0.0412	0.229
Average, 18	0.0455	0.258

The per cent residual fat lost varies from 0.103 to 0.332 excepting in determination 83, which is 0.516



FIG. 2 Showing the Modified Babcock Test, Bottles, and Holder. The test bottle to the right shows a factory control test.

Bottom of fat column dim, indicated by arrow

per cent. The amount of milligrams of fat lost varies from 18.5 to 59.0 and 93.0, which one is considerable above the others. The average per cent residual

¹ Indiana Agr. Exp. Sta. Bull. 145, p. 570.

summarized in Table VI. The results from samples A and B being satisfactory, another known mix was weighed out in grams, as follows, on a laboratory balance sensitive to 0.01 gram:

	Grams
Cream at 21.1 per cent.....	340.02
Sugar.....	68.25
Vanilla extract.....	2.295
Total mix.....	410.57

equivalent to 14.47 calculated per cent butter fat. This was divided into two parts, samples E and F. Sample F was frozen. Results are given in Tables VI and VII.

TABLE VII—SUMMARY OF TABLE VI

Mix and No. of detns.	Low with calculated per cent		Maximum variation	
	Standard reading	Direct reading	Standard reading	Direct reading
Mix "A" av. 13 detns...	0.22	0.50
Mix "B" av. 10 detns...	0.26	0.50
Mix "E" av. 8 detns...	0.37	+0.03	0.50	1.00
Mix "F" av. 10 detns...	0.37	0.26	0.90	0.90
Total detns. 41	0.305	0.145	0.60	0.95

The results of samples A and B are, on an average of 13 determinations, 17.53 per cent and from 10 determinations 17.49 per cent, respectively. A and B compared with the calculated per cent 17.75, are low, 0.22 and 0.26 per cent, respectively. 17.51 is the average per cent for the total 23 determinations. This is 0.24 per cent low with the calculated quantity of fat.

On 8 determinations from sample E an average of 17.10 per cent and on 10 determinations, standard readings on sample F, also 17.10 per cent were obtained. The direct readings in comparison with the standard readings were somewhat higher, being 17.51 and 17.21 per cent, respectively, the calculated per cent being 17.47. On a total of 18 determinations an average of 17.16 per cent or 0.31 per cent low with the calculated amount was obtained.

The per cent fat low in comparison with the calculated per cent (see Table VII) on samples A, B, E, F was respectively 0.22, 0.26, 0.37, 0.37. It is important to observe that with the direct reading (which

	Grams
"A" Cream at 20.5 per cent.....	441.5
Sugar.....	83.3
Vanilla extract.....	2.0

Calculated per cent butter fat, 17.02 for 531.8 grams
Roese-Gottlieb M. per cent butter fat, 17.03 on 3 determinations

is of more interest to practical ice cream makers), the per cent fat low for E and F was less, being $+0.03$ and -0.26 , respectively. The maximum variation, however, is somewhat greater than with the standard reading.

The maximum variation for A, B, E, and F varied from 0.50 to 0.90. The average per cent of fat for a total of 41 determinations is 0.305 low in comparison with the calculated per cent and has a maximum variation of 0.60. For the direct reading the average per cent of fat low is less by one-half that of the standard reading (Table VII), while the maximum variation is greater.

SUMMARY OF AVERAGES OF FAT BY THE MODIFIED BAB-
COCK COMPARED WITH THE ROESE-GOTTLIEB
METHOD ON SAMPLES 10/26/12,
11/19/12 AND 11/9/12

TABLE VIII—COMPARISON OF MODIFIED BABCOCK WITH ROESE-GOTTLIEB METHOD ON SAMPLE 10/26/12

Detn. No.	Modified Babcock. Standard reading	Det. No.	Roose-Gottlieb method
1.....	14.0	1.....	14.55
2.....	14.28	2.....	14.94
3.....		3.....	
4.....	14.66		
Averages.....	14.31		
Maximum variation.....	0.66		
Low. per cent fat.....	0.44		

Having obtained good results so far, it was determined to check this method with the Roese-Gottlieb on three samples. The first sample, 10/26/12, is a preliminary mix compared with the Roese-Gottlieb method.

By the proposed method, 14.31 per cent of fat is obtained from 3 determinations while with the Roesse-Gottlieb method this is 14.75 per cent fat. The Modified Babcock runs 0.44 per cent low. The maximum variation for the Modified Babcock and the Roesse-Gottlieb methods are, respectively, 0.66 and 0.39 per cent.

Next two mixes were carefully weighed out on a laboratory balance sensitive to 0.01 gram, as follows, numbered sample 11/9/12:

	Grams
"B" Cream at 20.2 per cent.....	441.5
Sugar.....	83.3
Vanilla extract.....	2.7

Calculated per cent butter fat 16.75 for 532.50 grams
Roese-Gottlieb per cent, 17.11 on 3 determinations

TABLE IX—SUMMARY OF AVERAGES OF FAT BY THE MODIFIED BABCOCK COMPARED WITH THE ROESE GOTTLIEB METHOD ON SAMPLES 10 26 12, 11 9 12 AND 11/19/12

Sample No.	Roese-Gottlieb		Modified Babcock			Proposed test low with R.-G.		Calculated per cent. fat		Max. variation		
	No. of detns.	Fat. Per cent.	No. of detns.	Standard reading	Direct reading	Standard reading	Direct reading	In sample	Low with R.-G.	Modified Babcock		
										Standard reading	Direct reading	R.-G. method
10/26/12.....	2	14.78	4	14.31		0.44		14.9	+0.15	0.66		0.39
11/9/12. { Part "A".....	3	17.03	14	16.67	16.96	0.36	0.07	17.02	0.01	0.70		0.02
{ Part "B".....	3	17.11	10	16.20	16.66	0.91	0.45	16.75	0.36	0.79		0.03
11/19/12.....	3	17.48	16	16.74	17.31	0.74	0.17	17.28	0.20	0.80	0.75	0.38
Average.....			44			0.60	0.17		0.11			

Sample 11/16/12 was taken directly from the freezer in the University creamery room. The calculated per cent fat, the data showed, was 17.28; the per cent fat by the Roese-Gottlieb from three determinations averaged 17.48; the average per cent fat by the Modified Babcock on 16 determinations is 16.74.

Thus from the summary (Table IX) it is seen that the test runs low with the Roese-Gottlieb method from an average of 0.44 per cent to 0.91 in sample B, which was sampled after long standing. Also the variation in sample 11/19/12 was greater. It is seen that the maximum variation for the Roese-Gottlieb method is 0.39 and 0.80 per cent for the Modified Babcock, or twice as great.

On the average of 44 determinations, the Modified Babcock runs 0.60 per cent low and by the direct reading 0.23 per cent. The calculated reading here ran close to the Roese-Gottlieb, an average of 0.11 per cent low.

PROPOSED MODIFIED BABCOCK METHOD IN DETAIL

To an 18-gram charge add the usual sulfuric acid (1.82-1.83 sp. gr.) in small portions of 3 cc. at a time, shaking after each addition with a slight pause. Continue adding acid in portions till a light amber-brown color or the *color of coffee with cream* in it, is obtained. Stand a few moments. Then check the action of acid with 5 cc. of cold water with shaking. (This should be done before the solution becomes a *deep dark brown* or blackish color, which shows charring action on the sugar—which precipitate, if formed, is difficult to dissolve.)

The solution having the color of coffee with cream in it, centrifuge five minutes. Then add 5 cc. of boiling water, whirl one-half minute longer. Drain off the acid through the glass stopcock carefully by tilting the bottle (approximately 5 cc. of solution will be left).

Dilute with cold water up to 10 cc., shake. Add acid in small portions as above, with shaking (approximately 8 to 10 cc.), till the remaining curd is dissolved or an almost coffee-black color, as in testing milk, is obtained. Add 3 cc. excess of acid and shake. Whirl 4 minutes.¹ Dilute to the neck with an acid solution (3:5), 3 parts of the sulfuric acid to 5 of water, at a temperature of about 60°-70° C.

Whirl one minute. Then add boiling water up to zero or above and again whirl one minute more. Read the per cent of fat.

REMARKS ON THE METHOD

There were two obstacles which gave considerable difficulty in working out this method. One was an occasional curdy or flocculent precipitate beneath the fat column. On dilution with hot water, it was found that a part of the protein precipitated out and centrifuged into the neck as a flocculent precipitate. To avoid this an acid solution (1:1) of sulfuric was

¹ This method in factory control can be considerably shortened after the first draining by whirling 4 minutes, then adding the dilute acid mixture up to zero or above. Whirl two minutes more and read directly. The variation in the per cent of fat is slightly greater or lower by a few tenths.

used for dilution instead of hot water, being mixed as needed. This solved this difficulty and prevented any precipitate from interfering. However, with this modification it was noticed that at times an occasional test read high. It was also observed that this occurred when one-third or more of the lower part of the fat column was emulsified. When this was less than one-third no appreciable error was observed.

To overcome this difficulty, a weaker acid was necessary. An average of many determinations indicated that a strength of 3:5, three parts of sulfuric acid to five of water, gave good results. This was too hot at times and then slightly emulsified the lower part of the fat column. Therefore, on mixing the acid used, it was dipped in cold water, stirring till 60° to 75° C. was reached. This was used at once and the test gave no further trouble, neither a flocculent precipitate nor an emulsified fat column.

This test was worked out under such conditions that the color of the fat column was a light *walnut*, not a *golden* yellow, and by following the directions this should be obtained.

One hundred determinations were made in working out the preliminary test and a total of 350 tests in completing and substantiating the method. Commercial sulfuric acid, which was frequently used, gave no difficulty. A D. C. Electric twelve-bottle centrifuge of Creamery Package Mfg. Co. was used throughout. This tester was not electrically heated.

To keep the glass stopcocks from loosening, a rubber cement worked well. Caoutchouc was heated to melting. This was used sparingly.

SUMMARY

1. This is a rapid control method.
2. Results consistent with the Roese-Gottlieb method are obtained, though averaging 0.6 per cent. low.
3. The per cent. residual fat lost in the drained portion averages the same as that lost in cream testing.
4. The maximum variation of fat readings is not great considering that the variation is somewhat greater on samples which have stood some time and hence are not perfectly uniform. The variation with the Modified Babcock compares favorably with the Roese-Gottlieb method.
5. This method can be used in International centrifuges in food control laboratories if preferred, by using a separatory funnel with a graduated cream tube at the top. This method is also applicable to ice cream plants using the ordinary commercial sulfuric acid on hand. Likewise, a similarly modified ten per cent milk test bottle can be used for determining fat in sweetened condensed milk.

The author desires to express his acknowledgments for advice and facilities to C. H. Eckles, Professor of Dairying, also to Dr. P. F. Trowbridge, of the Department of Agricultural Chemistry, of the Univer-

sity of Missouri, and to Mr. O. C. Smith, of the Experiment Station, for glassblowing.

MISSOURI DEPARTMENT OF FOOD AND DRUG INSPECTION
COLUMBIA

SAMPLING ICE CREAM¹

By J. O. HALVERSON

In an investigation on the Modified Babcock² for testing sweetened dairy products, especially ice cream, considerable variation in the results for butter fat was at times obtained. It did not appear that this was caused by the tests used as it was observed in both the Modified Babcock and the Roese-Gottlieb methods.

Thus it was necessary to investigate the factors which influence the per cent of milk fat obtained. These results are discussed in this paper.

A good quality of ice cream, testing 16 to 17 per cent fat, was used. This was made in the University creamery room under the best of conditions. A fact of some importance is worth mentioning in this connection: A small amount (about a tablespoonful) of commercial ice cream powder (gum tragacanth in part) was used as a thickener in the formula for standard vanilla ice cream, given below.

An intermittent Miller-Tyson Co.'s freezer, of capacity 20 gallons per hour, was used.

This, in larger amounts, may have some effect in preventing the "churning" of fat in ice cream. However, this was not investigated.

Formula for 5 gallon mix:

30 lbs. cream at 21 per cent
6 lbs. sugar
60 cc. vanilla extract
Small amount, ice cream powder

In Table I, fat readings in the Modified Babcock Method, taken at 130° to 140° F. with glymol, are designated "standard readings," while those taken at once upon completing the test, are given as "direct readings."

Considerable variation in results at times obtained, may be caused by a non-uniformity of the ice cream itself or poor mixing after having stood several days in the cooling room. This subject therefore divides itself into three parts:

1. Non-uniformity of the ice cream itself.
2. Effect of testing charges taken at different times on ice cream samples which have stood, allowing the cream to rise to the top.
3. Method of mixing ice cream samples after having stood some time.

NON-UNIFORMITY OF THE ICE CREAM

At all times the cream was carefully mixed, special care being taken to prevent churning. All charges in each set in Table I were weighed out at the same time. Occasionally some variation seemed due to an unavoidable non-uniformity of the cream itself. A rich cream, as here worked with, is liable to churn to a slight extent in the freezer and contain at times small lumps of butter; such were found. In weighing out charges

they obstructed the milk pipette. The freezer was examined after the day's run. A considerable number of small lumps of churned butter forming a layer estimated at one-eighth to three-sixteenths of an inch deep were found along the edges of the revolving paddles. This layer of small lumps of butter became more marked on the last batches frozen. These small particles of fat were more noticeable at times in the frozen cream. Thus hot weather and old cream may be more favorable for their formation than cold winter weather. These factors, however, were not studied.

EFFECT OF TESTING CHARGES TAKEN AT DIFFERENT TIMES ON ICE CREAM WHICH HAS STOOD, ALLOWING THE CREAM TO RISE TO THE TOP

Further work led to the belief that the charges were not uniform, due to the inability to thoroughly mix the samples after standing in the cooling rooms for several days. At the temperature of 40° to 50° F. in the cooling rooms on samples preserved with formalin, the cream in the ice-cream sample tended to rise to the top. To uniformly mix the sample in order to take charges for testing gave some difficulty.

On sample 11/19/12 are shown the results of three sets of charges taken as follows (each of these was checked up by the Roese-Gottlieb method).

TABLE I.—"SAMPLING" ICE CREAM. SAMPLE 11/19/12
Fat by Modified Babcock

	Determination number	Fat		
		Roese-Gottlieb	Standard reading	Direct reading
First set.	1	17.70	17.10	17.30
	2	17.56	17.10	17.35
	3	17.32	17.20	17.50
	4	...	17.00	17.25
	5	...	17.00	17.30
Second set	6	17.07	16.15	16.25
	7	16.91	16.30	16.30
	8	...	17.10	17.25
	9	...	16.80	16.85
	10	16.45	17.00	16.85
Third set.....	11	17.18	16.60	16.80
	12	16.75	16.50	16.75
	13	...	16.75	16.90
Average. Dets.	8	17.09	13—16.79	13—16.94
Maximum variation.		1.25	1.05	1.25
1st set (sampled at once), av.		17.48	17.38	17.34
2d set (sampled 1 week later), av.		16.99	16.59	16.64
3d set (sampled still later), av.		16.79	16.71	16.83
Max. variation, 1st set.		0.38	0.10	0.25
Max. variation, 2d set.		0.16	1.65	0.45
Max. variation, 3d set.		0.73	0.50	0.15

First Set.—Determinations one to five were tested at once from the sample as the ice cream came from the freezer.

Second Set.—Determinations 6 to 9 were taken 1 week later from the same sample, using particular care to obtain as uniform charges as possible.

Third Set.—Determinations 10 to 13 were charges taken still later and tested.

From the averages and maximum variation on each set it will be seen that when sampled at once the highest per cent of fat is obtained. Also that, in general, the variation on individual determinations was small while in the third set (determinations 10 to 13) it is observed the average per cent of fat is lower by both

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913.

² "The Modified Babcock for Fat in Sweetened Dairy Products—Ice Cream," *THIS JOURNAL*, 5, 403.

the Reese-Gottlieb and Modified Babcock method. The maximum variation on the three sets is considerable by both methods, showing that it is somewhat more difficult to obtain as uniform results as are obtained on fresh samples unless they have been kept at or below freezing temperature.

To eliminate this difficulty as much as possible, 18-gram charges are used. The method of mixing ice cream samples after standing some time was also given careful attention.

METHOD OF MIXING ICE CREAM SAMPLES AFTER STANDING SOME TIME

Ice cream samples which have been kept in a refrigerator or in cooling rooms for some time are not readily sampled for uniform charges unless some precautions are taken. This is especially necessary when the ice cream has melted somewhat and the cream risen to the top, forming a layer. Thus to obtain a uniform charge, the author found it convenient to dip the sample jar in a pan of hot water at about 70° to 80° C. with gentle shaking, until it had approximately attained the temperature, as felt by the hand, of freshly drawn milk (98° F.). Carefully shake and mix until of a uniform consistency. This occurs and will be shown when the mixture runs freely down the sides of the glass container and no lumps are seen.

There is danger of the fat separating and rising to the top of the sample if it is heated too long or much above 80° C. This condition makes uniform sampling impossible and is to be avoided.

SUMMARY

1. The ice cream itself may not be perfectly uniform. This may not be noticeable except on the paddles of the freezer. The extent of "churning" in these samples was, of course, small.

2. In taking charges from preserved ice-cream samples which have stood in a cooler so that the cream rises, not perfectly uniform charges can be obtained. This, it appears, causes a slightly greater variation in the fat reading with a tendency to run somewhat lower.

3. The mixing of ice-cream samples should be carefully performed, especially when they have stood so that the cream has risen to the top.

MISSOURI DEPARTMENT OF FOOD AND DRUG INSPECTION
COLUMBIA

SOME EFFECTS OF FEEDS UPON THE PROPERTIES OF LARDS. II

By C. L. HARE

Received April 8, 1913

In a former paper¹ the writer described the effects of a number of different feeds upon the melting points and iodine values of lard. In the present paper are given results obtained during the examination of more than two hundred lards produced by feeds of different kinds. The lards are from six series of feeding experiments extending over a period of five

years and have been furnished by the Department of Animal Industry of the Alabama Experiment Station. These investigations have been conducted in cooperation with Prof. Dan T. Gray, of that department.

In continuing the investigations, attention has again been confined largely to melting points and iodine values as these are the two constants—so called—most affected by different feeds. The feeds used have been corn, cottonseed meal, tankage, wheat shorts, cowpeas and skim-milk for certain lots, while still other lots received a pasture ration of soy beans or peanuts *ad libitum*, accompanied or followed by a part ration of other feeds as indicated in the tables. In order to have the results comparable, the pigs throughout the experiment were selected with regard to uniformity of age, weight and breed, and all lards were rendered from the kidney fat.

For purposes of convenient comparison, the results published in the first paper have been placed beside the later results. The feeds used with each separate lot of pigs in each series are specifically set out in the tables of results. Results on the individual lards in each series have been condensed to the averages for the series and the tables show such averages. Each series represents the experimental work of one year.

It will be shown below that—within reasonable limits—the age of the pig has little effect upon the properties under consideration. The same may be said of the duration of the feeding test, though this is not true for all feeds. We are therefore warranted in accepting the average results as representative. Results reported on individual lards would merely multiply figures without giving additional information.

In every case melting-point determinations were made by the Wiley method while the Hanus method was used for the determination of the iodine values.

Lards from corn-fed pigs constitute the bulk of the pure lard on the market and are used here as the standard for comparison of lards from other feeds. In Table I are given results on lards from twenty corn-fed pigs.

TABLE I—RATION: CORN MEAL

Series	No. of lards	Melting points	Iodine values	
			Max.	Min.
1.....5	42.6	56.92	58.68	53.87
2.....5	43.7	54.05	56.57	51.50
3.....3	43.4	62.65	64.79	60.07
4.....2	43.3	57.01	57.87	56.16
5.....5	42.6	60.94	65.04	54.00
Average of 20 lards,	43.1	58.08		
Maximum	45.6	65.04		
Minimum	40.5	51.50		

The iodine value 58.08, being the average of determinations on lards from 20 pigs, confirms the conclusion in the previous paper that corn does not produce abnormally soft lards. The variations in the iodine values from year to year may be possibly, though not probably, explained by variations in the composition of the corn. No analysis was made of the corn

¹ THIS JOURNAL, 2, 264.

fed. The differences due to the individuality of the animal are well known and the maximum and minimum results in each series show no greater divergence than might be expected.

Tables II and III illustrate the notable effect of cottonseed meal upon the melting points and iodine values.

TABLE II—RATION: CORN 2/3, COTTONSEED MEAL 1/3

Series	Number of lards	Melting point	Iodine value	
			Max.	Min.
1.....6	48.6	56.14	61.00	53.57
2.....4	49.9	50.37	51.60	48.44
Average 10 lards,	49.1	53.83		

TABLE III—RATION: CORN 9/10, COTTONSEED MEAL 1/10

Series	No. of lards	Melting point	Iodine values	
			Max.	Min.
2.....5	48.7	52.85	53.80	50.60
3.....1	48.4	49.23		
4.....4	49.1	55.31	60.56	51.28
Average 10 lards,	48.8	53.47		

A review of the figures in the two tables indicates that a high cottonseed meal ration produces no greater changes in the characteristics of the fat than does a low ration of this feed. Both tables might well be grouped in one. The average of the melting points of the 20 cottonseed meal lards is about 6° C. higher than the average for the 20 corn lards, while the iodine values average nearly five points lower.

Another high protein ration which contributes to lards properties similar to those conferred by cottonseed meal is tankage.

In Tables IV and V are found results on 39 lards from pigs fed on a ration made up in part of tankage.

TABLE IV—RATION: CORN 4/5, TANKAGE 1/5

Series	No. of lards	Melting point	Iodine values	
			Max.	Min.
4.....4	44.5	57.08	63.98	52.75
4a.....5	43.7	57.52	60.16	52.70
5.....3	44.1	56.15	59.22	54.28
Average 12 lards,	44.1	57.03		

TABLE V—RATION: CORN 9/10, TANKAGE 1/10

Series	No. of lards	Melting points	Iodine values	
			Max.	Min.
1.....5	43.6	56.46	59.08	50.06
2.....6	42.5	55.15	58.80	49.85
3.....4	44.4	56.04	61.29	52.26
4.....25	43.5	57.85	71.79	53.48
5a.....7	44.8	56.89	65.04	54.54
Average 27 lards,	43.9	56.58		

This ration produces scarcely so great a hardening effect upon the lards as does cottonseed meal. In fact there is no great difference between the lards produced from corn alone and those from corn with tankage. The tankage lards have a better appearance and are somewhat firmer, despite the nearness of the melting points and iodine values of the two sets. As was the case with cottonseed meal, small quantities of tankage in the ration—within the limits used—seem to bring about almost as great changes in the properties as do larger amounts.

The influence of still another ration relatively high in protein, cowpeas, was tested in one series of feeding experiments. Three pigs were slaughtered from

a ration of corn and cowpeas. The number of pigs is too small to justify definite conclusions, but the results are given below:

TABLE VI—RATION: CORN 4/5, COWPEAS 1/5

Series	Lab. No.	Melting point	Iodine values
5.....	160	42.9	60.86
	161	44.8	53.95
	165	42.2	58.23
Average, 43.3			57.35

In this experiment there was also carried a lot of five pigs pastured on corn and cowpeas.

The results on lards from these pigs are shown in Table VII:

TABLE VII.—RATION: PASTURE OF CORN AND COWPEAS

Series	Lab. No.	Melting point	Iodine values
5a.....	1	45.4	53.95
	2	42.5	57.42
	3	44.8	56.59
	4	43.0	56.59
	44	46.4	57.25
Average 5 lards,		44.4	56.36

These figures confirm other experiments which indicate that cowpeas contribute firmness to lards. It was thought that the pastured corn and peas would perhaps yield softer lards than the same ration fed as grain, but the lards from the two rations possess essentially the same properties. The average of the melting points and iodine values of the eight lards is 44 and 56.73. These results are nearly the same as the corresponding results for the 20 corn lards, the slight differences being in favor of the lards from the cowpea ration.

In Table VIII are given some inconclusive figures illustrating the effect of wheat products:

TABLE VIII—RATION: CORN 2/3, WHEAT SHORTS 1/3

Series	Lab. No.	Melting point	Iodine values
4.....	2	42.0	59.51
	17	41.5	60.00
	16	42.8	58.26
	67	43.4	57.29
Average,			58.74
5.....	166	41.6	65.40
	176	40.0	64.02
	180	40.3	63.96
	181	40.1	64.02
5a.....	183	42.0	62.64
			Average, 64.00
5a.....	4	43.9	57.25
	1	44.3	56.23
Average, 56.74			
Average 11 lards,		42.4	60.78

It is probable that the results in Series 4 and 5a represent most nearly the true effect of the wheat in the ration. The average iodine value of the lards in these two series is practically the same as that of the 20 corn lards. Those in Series 5 are unquestionably high. Three of the corn lards in this series gave an average iodine value of 64.70. No attempt is made to explain these abnormally high figures. As has already been suggested, there may be some connection between them and the composition of the corn used in the feeding experiments of that year. Although such necessarily slight differences as would occur in the composition of corn from different sections or of

different years growth would hardly be expected to make so great a difference in the characteristics of the lards produced therefrom. In this connection it is noted that the pigs in each series of the corn and shorts experiments received corn from different sources.

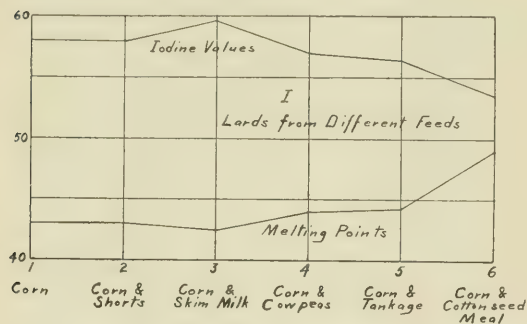
The effect of skim-milk in producing firm pork and firm lard is well known. The figures in the following table are in accord with previous results on lards produced by a ration containing that food:

TABLE IX RATION: CORN 1 LB., SKIM-MILK 2 1/4 LBS.

Series	Lab. No.	Melting point	Iodine values
5	119	43.0	58.26
	177	42.8	57.92
	179	40.3	65.40
	182	42.8	57.25
Average		42.2	59.71

No. 179 yielded abnormal results, which may be explained by individual characteristics of the pig.

In Chart No. 1, below, is shown the course of the curves of the iodine values and melting points of lards from the six feeds considered to this point, using the corn lards as the standard.



The curves represent the assembled results obtained from 97 lards, all of which were examined under similar conditions. They constitute a good illustration of the relative courses of the curves for melting points and iodine values. It is probable that the curve of the skim-milk lards does not represent a normal lard produced by that feed, as the iodine values are perhaps too high for such a lard. The striking effect of soy beans in producing oily lards is shown in the three following tables:

TABLE X—RATION: SOY BEAN PASTURE AND CORN 1/4 RATION

Series	Lab. No.	Melting point	Iodine value	Feeding period Days
2	34	...	100.50	35
3	76	...	94.86	75
4	10	...	113.31	81
Average 3 lards			102.89	

TABLE XI—RATION: SOY BEAN PASTURE AND CORN 1/2 RATION

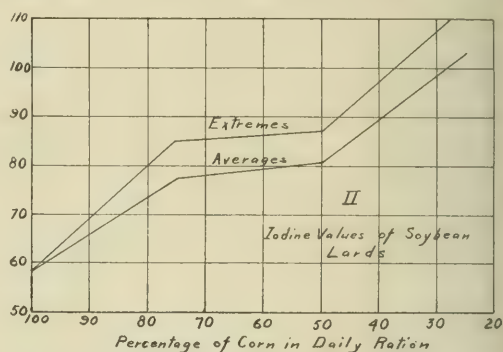
Series	Lab. No.	Melting point	Iodine value	Feeding period Days
1	125	...	71.09	35
2	23	...	80.60	35
3	87	...	82.70	75
4	23a	...	86.20	81
Average 4 lards			80.18	

TABLE XII—RATION: SOY BEAN PASTURE AND CORN 3/4 RATION

Series	Lab. No.	Melting point	Iodine value	Feeding period Days
2	15	...	79.00	35
3	68	...	84.32	75
4	35	...	65.69	81
Average 3 lards			76.34	

Inspection of the three tables reveals the fact that soy beans yield lards with much higher iodine values and degrees of fluidity than have been found recorded in the literature of the subject. Only a small amount of solid fat separates from the lard possessing an iodine value of 113.31.

The results further show in a striking manner that diminishing the corn ration rapidly increases the oiliness of the lards. This is well illustrated in the curves charted below. The curves also illustrate the remarkable effect of this food in producing fats containing large amounts of unsaturated acids.



The value of corn as a corrective for oiliness is further demonstrated in the following table, which includes (1) lards from one lot of pigs off soy bean pasture and 1/4 ration of corn and (2) lards from a second lot fed on the same ration for the same length of time but afterwards finished on corn:

TABLE XIII—PRELIMINARY RATION: SOY BEAN PASTURE AND 1/4 CORN

Series	No. of lards	Melting points	Iodine value	Finishing ration	Feeding period Days
2, 3 and 4	3	...	102.89		35-75
3 and 4	7	40.7	75.24	corn	28-73

The pigs on the preliminary ration produced extraordinarily soft lards. Following this a full corn ration has, at the end of one month, materially hardened the fat, and the average iodine values of the 7 lards from pigs finished on corn is 25 per cent lower than that of the soy bean lards. The hardening effect on lards of cottonseed meal as a finishing ration for pigs pastured on soy beans is not as striking as would be expected from results on lards produced from a simple ration of corn and cottonseed meal. Comparative figures are given in Table XIV.

TABLE XIV—PRELIMINARY RATION: SOY BEAN PASTURE AND 1/4 RATION OF CORN

Series	No. of lards	Melting point	Iodine values	Finishing ration	Feeding period Days
2, 3 and 4	4	...	80.18		35-81
3 and 4	4	45.2	72.61	corn and cottonseed meal	28-64

Cottonseed meal in the finishing ration seems, in this case, to have no greater influence in changing the nature of the fat than does corn. The same statement may be made with regard to tankage and is borne out by the figures given below:

TABLE XV—PRELIMINARY RATION: SOY BEAN PASTURE AND 3/4 RATION OF CORN

Series	No. of lards	Melting point	Iodine values	Finishing ration	Feeding period Days
2, 3 and 4.....	3	76.34	corn and tankage	35-81
3 and 4.....	7	42.5	71.93		35-75

It was to be expected that either cottonseed meal or tankage in the finishing ration would have influenced the properties of the lards more decidedly than corn as the finishing ration. Such would probably have been the case if the fats finished on these rations had been as strikingly soft as the fats finished on corn.

The softening effect of peanuts is well known. The relative effects of soy beans and peanuts is in some measure indicated by the figures in Table XVI. The first lot of 10 lards are from pigs slaughtered from soy bean pasture and a part ration of corn. The second lot of three lards are from pigs fed the same ration followed by peanut pasture and 1/2 ration of corn.

TABLE XVI			
No. of lards	Melting point	Iodine values	Ration
10	85.84	Soy beans and corn 35 days
3	85.49	{ Soy beans and corn 35 days Peanuts and corn 35 days

These figures would seem to indicate that peanuts have nearly the same effect as soy beans. The physical appearance of the lards in the two sets is much the same, all being nearly fluid or semi-fluid. Investigation showed that the properties of such lards may be readily changed under the influence of rations of corn, cottonseed meal or tankage.

This is indicated by the figures given in Table XVII.

TABLE XVII—PRELIMINARY RATION: SOY BEAN PASTURE AND PART CORN 35 DAYS, FOLLOWED BY PEANUT PASTURE AND PART CORN 35 DAYS

Series	No. of lards	Melting point	Iodine values	Finishing ration	Feeding period Days
2.....	4	85.49	corn	14-64
2.....	3	37.6	75.61		
2.....	3	41.2	75.64		
2.....	3	41.5	72.26	corn and cottonseed meal	14-64
				corn and tankage	15-64

Only the averages of the three lards in each set are given. The melting points and iodine values of the individual numbers in each set indicate increasing firmness with length of time fed, the greatest relative increase being noted in the first fourteen days. It may be said here that this is true in every case where a ration is used to finish and firm the fat.

Throughout these experiments observations have been made as to the influence of age of the pig upon the properties of lard. It is perhaps the general belief that young pigs yield lards which vary materially in properties from those produced from older animals. Records have been kept upon lards from 85 pigs varying in age from four to eight months at time of

slaughtering and the results seem to indicate a fair degree of uniformity in the lards produced by the same feeds, without regard to age of the animal. The influence of age can scarcely be measured where such feeds as soy beans and peanuts have been used as they produce lards which are in every respect abnormal. Detailed results on the 85 lards are set forth in the following tables. The lards are grouped in each table in accordance with feed from which they were produced:

TABLE XVIII—CORN LARDS															
AGE OF PIG															
4 mo.				5 mo.				6 mo.				7 mo.			
M.	P.	I.	Val.	M.	P.	I.	Val.	M.	P.	I.	Val.	M.	P.	I.	Val.
43.1	56.50	43.5	53.87	43.4	58.68	44.2	57.60	41.6	57.37	44.8	51.50	44.0	49.70
....	42.8	64.79	42.1	57.87	44.4	63.08	43.0	60.07
....	45.6	53.98	44.5	56.16
....	43.0	58.56
....	41.5	64.98
....	43.2	65.04
....	40.5	64.02
....	42.0	59.28
Av.	43.1	56.50	43.8	56.69	43.8	55.06	43.0	60.52	41.7	57.77

TABLE XIX—CORN AND COTTONSEED MEAL LARDS															
47.7	61.00	49.8	53.57	49.3	53.57	48.3	57.58	50.0	55.16
49.2	48.44	50.8	51.20	49.6	50.22	46.8	55.95
....	48.6	53.80	50.0	51.60	47.6	55.00	49.0	52.00
....	48.4	50.60	48.8	56.89	48.8	60.56
....	48.4	49.23	49.1	52.50
....	49.6	51.28
Av.	48.5	55.31	49.7	52.86	49.2	51.22	48.7	54.44	48.7	55.92

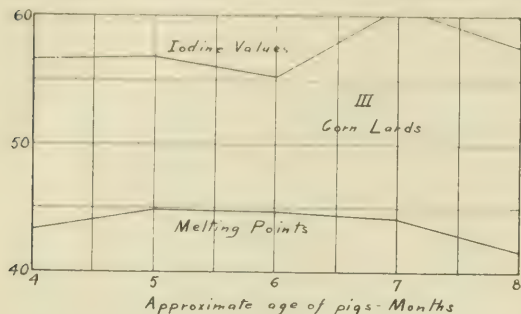
TABLE XX—CORN AND TANKAGE LARDS															
43.1	59.08	45.6	50.06	42.5	56.59	41.6	57.80	45.1	57.77
....	49.85	43.0	56.80	42.9	56.53	42.6	61.29	45.4	53.61
47.2	55.21	43.0	57.92	42.2	52.40	44.5	52.26	41.3	63.98
44.4	54.54	44.9	54.86	41.4	58.80	44.9	55.67	42.0	61.17
43.1	65.09	45.0	55.56	45.1	57.02	45.9	52.75	43.3	57.78
46.2	54.88	45.9	55.92	45.3	53.48	43.6	59.77
....	45.7	56.41	40.9	60.32
....	44.0	54.28	46.0	52.70
....	43.8	57.29
....	41.6	60.16
....	43.3	54.94
....	45.0	59.22
....	56.53
Av.	44.8	56.44	44.3	55.04	43.7	56.00	43.8	56.60	43.5	59.01

TABLE XXI—CORN AND SHORTS LARDS															
43.9	57.25	44.3	56.23	42.0	59.61	42.8	58.26	43.4	57.29

It is seen from the results on the individual lards as well as from the averages, that pigs eight months old yield lards with essentially the same melting points and iodine values as those from pigs four months old. The number of four-month old pigs in each set is small but the total recorded number is 10 and only two lards in the lot of ten show higher iodine values than the lards from older pigs in the same sets. The influence of age is well illustrated in the curves plotted in the charts on page 414.

In addition to the study of influence of age, the following notes have been made upon the effect of high, medium and low protein rations upon the lards produced from each. The feeds were made up so as to contain about 10 per cent, 15 per cent, and 20 per cent protein. Results on the lards from low protein rations are not altogether comparable with those from the medium and high protein rations for the reason that the nature of the feed furnishing the protein

is different. However, the results on the medium and high protein feeds are entirely comparable, as

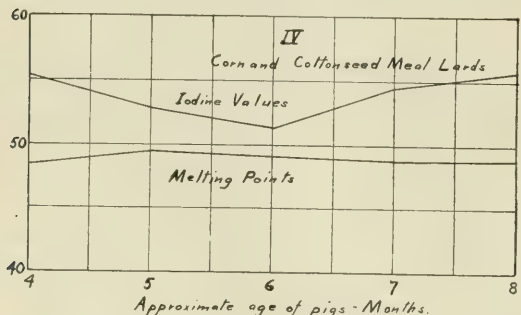


the same food materials were used in mixing the rations. Lards from 77 pigs have been tabulated.

TABLE XXII—LARDS PRODUCED FROM HIGH, MEDIUM AND LOW PROTEIN RATIONS

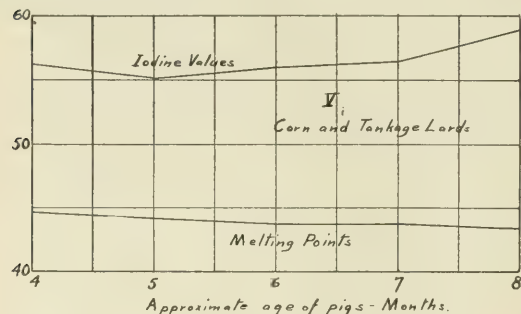
Percentage of protein	No. of lards	Melting point	Iodine values	Ration
10	20	43.1	58.08	Corn
10	5	42.8	58.09	Corn and shorts
15	10	48.7	52.47	Corn and cottonseed meal
20	10	49.3	53.15	Corn and cottonseed meal
15	25	43.9	56.58	Corn and tankage
20	12	44.1	57.03	Corn and tankage

Comparing the 10 per cent protein rations with the others, it is found that the melting points are



lower and the iodine values higher than in the other sets. This, however, is to be expected from the nature of the feeds used.

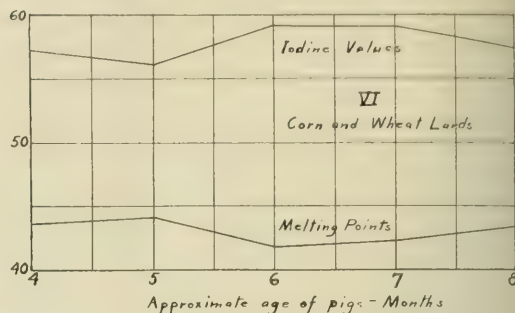
Examining next the medium and high protein rations, comparison shows that lards from a 15 per



cent protein ration composed of corn and cottonseed meal possess essentially the same melting points and

iodine values as do the lards from a mixture containing 20 per cent protein from the same source. The same is found to be true of lards produced by 15 per cent and 20 per cent protein rations made up from corn and tankage.

Before making any positive statements it would be



desirable to secure results from a series of experiments designed to include a larger number of rations with varying amounts of protein from the same source. The data recorded, however, strongly indicates that the amount of protein in the feed has little influence upon the properties here studied.

SUMMARY

A general review of the information here presented leads to the following conclusions:

1. Corn, and mixed feeds containing corn with wheat shorts, skim-milk, or cowpeas, produce fats which possess like properties.

2. Tankage produces a slightly firmer fat, while cottonseed meal produces fats which contain small amounts of unsaturated acids and which may remain solid at temperatures of 100° F. or above.

3. The two legumes, soy beans and peanuts, produce lards which contain extreme amounts of unsaturated acids and are fluid at ordinary temperatures.

4. Fats change in composition with remarkable readiness under the influence of certain feeds, small amounts of these feeds producing striking changes in the properties of the fats.

5. Between the ages of four months and eight months, age of the animal has essentially no influence upon the properties of the lard.

6. Using feeds differing as much as 5 per cent in protein content, there is observed no change in the properties of the lards produced therefrom.

7. With the advent of the various new feeds used in pork production, the iodine absorption number of a lard possesses no value as a means of detecting adulteration.

Acknowledgment is made to G. H. Marsh and J. B. Jackson, of this laboratory, for the large amount of analytical work performed during these investigations.

ALABAMA POLYTECHNIC INSTITUTE
AUBURN

FERTILIZATION OF CITRUS SOILS

By ALFRED SMITH AND H. E. BILLINGS

Received Feb. 17, 1913

When one considers the amount of fertilizer used in the various states and that the greater percentage of it is applied to the soil without due regard for the various factors influencing crop production, one feels that the returns do not justify the initial expense. Many experiments have been reported showing what injurious ingredients may be found in irrigation water or soil solution, but very little work has been done with respect to possible beneficial ingredients in the water before it reaches the soil which it is to irrigate. Of the many reports of the State Experiment Stations which deal with the analysis of water to be used for agricultural purposes few can be found which report any of the chemical elements at present considered of vital importance to plant life—such as potash, phosphoric acid, nitrogen and lime.

Since the year 1890¹ considerable work has been done in this state on alkali waters and occasionally one may find analyses showing the percentage of essential plant foods.² From records kept by individuals for several years it has been found that certain types of fertilizers have not responded as quickly, if at all, as have others; and it was to study some of the factors which bring such conditions about that led to the investigation of the quality of the irrigation water in this locality.

The region studied is in the extreme eastern part of Los Angeles County, California, and is devoted almost entirely to citrus culture. In the southern part, on account of the presence of alkali, only certain crops such as alfalfa and sugar beets are grown. The soil had been derived mainly from the metamorphosed granite ridges bordering the northern edge of the valley, along the foothills of which we find a very coarse gravelly sandy soil; as we proceed to the southern boundary the soil texture gradually changes until we have a very fine clay. According to Holmes³ the soil covering the northern portion of the area (60 square miles) contains 15.00 per cent. of silt and clay while that covering the southern portion contains 57.00 per cent. of silt and clay. All over the region one can recognize the presence of the following minerals—orthoclase, microcline, biotite, muscovite, calc spar and quartz. The water used in irrigation is obtained from the largest canyon in this vicinity (San Antonio) which is among the granitic ridges already referred to.

On making an analysis⁴ of this canon water at various times the following amounts of potash were found:

POTASH (K₂O) CALCULATED AS PARTS PER MILLION

Date	Amount
October 7, 1912.....	7.98
November 7, 1912.....	5.81
December 10, 1912.....	6.20

Having obtained these results, we were led to further investigation, as this water was used in different parts of the valley for the irrigation of citrus trees.

Some of the water is pumped for a distance of approximately 4 miles from the canyon. It is used for irrigation and then finds its way through underground channels, occasionally approaching the surface and forming marshes, to the southern part of the valley, where, after evaporation, it leaves behind large amounts of alkali. As the water is thus used over and over again for irrigation the problem as to how its chemical nature is changed presented itself. In the following table is given the potash content of this water, samples of which were obtained at different pumping plants located from north to south:

PUMPING PLANT	1912	K ₂ O Parts per million
Mountain Avenue.....	November 7	7.30
	December 10	8.10
	January 10	7.28
Indian Hill.....	November 7	6.54
	December 10	6.89
Pomona.....	November 7	6.10
	December 10	5.88
Chino.....	November 7	6.80
	December 10	5.91

From this table it is evident that the potash content of the water is greater in the northern part of the valley than in the southern, or when first used for irrigation. Determinations are being made each month so that if possible the rate of change can be better calculated. Somewhat corresponding figures have been obtained in the determination of total solids.

PUMPING PLANT	DATE	TOTAL SOLIDS Parts per million
Mountain Avenue.....	July 3, 1912	231.60
	August 3, 1912	251.20
	October 7, 1912	251.30
	November 7, 1912	230.00
	December 10, 1912	241.00
	January 8, 1913	249.10
	October 3, 1912	220.60
Indian Hill.....	November 7, 1912	221.00
	December 10, 1912	220.70
	January 4, 1913	220.40
	September 3, 1912	215.40
Pomona.....	December 10, 1912	222.00
	January 8, 1913	229.00
	July 3, 1912	220.30
Chino.....	August 3, 1912	232.00
	October 5, 1912	219.60
	November 7, 1912	224.00
	December 10, 1912	221.80
	January 8, 1913	220.40

The general practice here is to use 1 miner's inch (head of four inches) to every 7 acres and from the analyses here given it is found that a soluble form of potash to the extent of at least 53 pounds to each acre is annually applied to the soil.

From the reports of the Florida and California Experiment Stations⁵ the amount of potash in the fruit of an orange averages 0.238 per cent. Calculating

¹ Appendix to the report for the year 1890—State Experiment Station, California, pp. 51, 57.

² Analysis of Mohave River Water, Analysis of Artesian Water at Chino, California State Report, 1890. Irrigation in Hawaii, Office of Experiment Station, Bulletin 90. Analysis of Gila, Salt and Colorado Rivers, Arizona Agricultural Experiment Station, Bulletin 53. The Quality of the Surface Waters of California, Water Supply Paper, U. S. G. S., No. 237.

³ Soil Survey of the San Bernardino Valley, Bureau of Soils, 1904.

⁴ Official Methods of Analysis, Bureau of Chemistry, U. S. Dept. of Agriculture, Bulletin 107. Analysis of Silicate and Carbonate Rocks, Dept. of the Interior, U. S. G. S., Bulletin 305. "Examination of Water," Mason.

⁵ Bulletin 58, Florida Experiment Station. Bulletin 66, Florida Experiment Station. Bulletin 93, California Experiment Station. Bulletin 88, California Experiment Station.

the average amount of fruit obtained, we find that the potash taken from each acre of soil by this type of citrus fruit averages 137 pounds. Referring back to the amount of potash annually offered to each acre of soil by the irrigation water we find that it is equal to 38.70 per cent of the amount that is taken from the soil by the fruit. Later papers will give results obtained with respect to other plant foods in the irrigation water.

The potash fertilization is not necessary where such an amount as stated above is offered by the irrigation water and where the soils are naturally rich in potash and where cultural experiments have shown negative results from potash fertilization where irrigation is practiced, we conclude that if the amount of potash in the water is as high as we have found there is no need of adding potash.

DEPARTMENT OF CHEMISTRY, POMONA COLLEGE
CLAREMONT, CAL.

THE EFFECT OF IGNITION ON THE SOLUBILITY OF SOIL PHOSPHATES

By G. S. FRAPS

Received January 20, 1913

Under the above title, Chas. B. Lipman presents, in *THIS JOURNAL*,¹ analyses of five soils, in which less phosphoric acid is dissolved by nitric acid after ignition than before ignition. The soils were digested with concentrated nitric acid for two days on the steam bath. He states: "We obtain, therefore, the very reverse effect of ignition on the soil phosphates as existing in the soil, from that obtained by Fraps on mineral phosphates as existing in minerals. In brief, ignition of the soil appears to decrease appreciably and definitely the solubility of its phosphates, whether they be largely inorganic or organic."

Contrary to the apparent opinion of the above author, it is not a theory but a well-established fact,² that ignition increases the solubility of the phosphoric acid of the soil in certain solvents, especially in cold concentrated hydrochloric acid. *Bulletin* 135 of the Texas Experiment Station contains determinations of the effect of ignition on the solubility of the phos-

phoric acid of 56 soils. In one group of ten soils, the quantity of phosphoric acid rendered soluble in cold hydrochloric acid by ignition, averages 0.0645 per cent. The effect of ignition on the solubility of soil phosphates in hot nitric acid, whatever it may be, will not alter the fact that ignition renders phosphoric acid of the soil more soluble in cold hydrochloric acid.

Ignition of the soil and solution in hydrochloric acid was proposed as a method for estimating the organic phosphoric acid of the soil.² In studying the matter the writer found that certain inorganic phosphates are not soluble in the cold hydrochloric acid, but are rendered soluble in it by ignition. It was also found that ignition increases the solubility of oxide of iron and alumina. This conclusion was, therefore, drawn:² "Ignition of the soil will probably render inorganic phosphates soluble in acid, and, therefore, is not a method for estimating organic phosphoric acid." If ignition decreases the solubility of the phosphoric acid of the soil in hot nitric acid, this fact does not show whether the phosphoric acid rendered soluble in cold hydrochloric acid by ignition is inorganic or organic. The phosphates rendered insoluble in hot nitric acid may have been either organic or inorganic before the ignition. The results obtained by this method, therefore, furnish no reason for modifying the conclusion given above. If the phosphoric acid of the soil is rendered by ignition less soluble in hot concentrated nitric acid, it by no means affects the fact that the phosphoric acid of the soil is rendered more soluble in cold concentrated hydrochloric acid. Since inorganic phosphates which may occur in the soil are likewise rendered by ignition more soluble in cold concentrated hydrochloric acid, and since the soil extracted with cold concentrated hydrochloric acid probably contains inorganic phosphates, we are justified in adhering to the conclusion that a portion of the phosphoric acid of the soil rendered soluble by ignition, is probably of inorganic origin. The fact that the phosphoric acid may or may not be rendered by ignition soluble in hot concentrated nitric acid, in no way affects the logic of this reasoning.

TEXAS EXPERIMENT STATION
COLLEGE STATION, TEXAS

LABORATORY AND PLANT

APPARATUS FOR THE PRECIPITATION OF BARIUM SULFATE UNDER UNVARYING CONDITIONS

By H. G. SMITH

Received March 17, 1913

On account of the difficulty experienced in trying to obtain uniform conditions for the precipitation of barium sulfate in a limited time I have devised a simple method that is not only satisfactory but also saves time.

The method consists in allowing a solution of barium chloride to run into a given sulfate solution drop by drop from a dropper, *A*, after the solution has been

heated so as to boil vigorously with the dropper containing the barium chloride solution in the position shown by the dotted lines *B*.

The dropper is made by bending an ordinary $\frac{5}{8}$ -inch test tube up at an angle of about 45 degrees one and one-half inches from the open end, drawing out the lower side of the bend with pinchers, breaking off the small tube *a*, formed near the end, and fusing the opening so that it will deliver about 80 drops per minute when in the horizontal position *A*. The upper part of the bend should be shaped so that somewhat of a ridge, *b*, is formed to allow air to readily

¹ Vol. 4, 663.

² Schmoeger, *Ber. d. chem. Ges.*, 26, 386; Aso, *Exp. Sta. Record*, 16, 555.

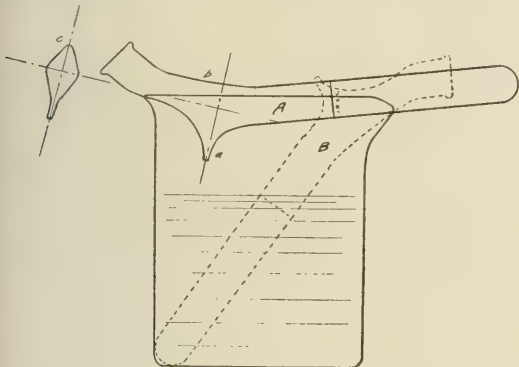
¹ Illinois Exp. Station, *Bull.* 145.

² *THIS JOURNAL*, 3, 335.

replace the barium chloride solution when flowing out. The tube at the dropping point then has the cross-section shown at *c*.

I think that it is unnecessary, especially when the solution contains only moderate amounts of sulfate, to stir during precipitation when using this dropper, as, the two solutions being at about the same temperature, the boiling continues vigorously, and further agitation is not required. The precipitation of barium sulfate in this manner requires no attention after the solution is set on the hot plate except to tip up the tube and to set aside to digest later, and one man can carry on a number of precipitations at one time.

In the determination of sulfur trioxide in cement in a limited time I obtain the best results under the following constant conditions: wt. cement, 2 grams;



hot water added, 30 cc.; conc. HCl added, 8 cc. (making about 3 cc. free acid in final solution or about 0.5 per cent. acidity); boiling 1 minute, filtering, washing twice; precipitating volume, 250 cc.; volume BaCl₂ solution, 10 cc. 10 per cent.; time adding BaCl₂ solution, about 2 minutes; time boiling after adding BaCl₂ solution, 5 minutes; time digesting, 1 hour; filtering; washing 5 times.

A series of fifty determinations of sulfur trioxide in cement made recently by this method gave the following results:

	Gram	Per cent. SO ₃
Average weight BaSO ₄ for series.....	0.0918	1.575
Weight BaSO ₄ from composite (1).....	0.0918	1.575
Weight BaSO ₄ from composite (2).....	0.0923	1.58

Although small amounts of barium sulfate can be recovered after several hours' standing from filtrates obtained after one hour digestion on hot plate, still results by the above method have always been found to be consistent, and to wait twelve hours or so in order to add a possible one-hundredth of one per cent. to a result seems unnecessary in technical work. If the above method were universally used there would probably be much closer agreement in the results of different analysts, especially in the cement industry.

THE TEXAS PORTLAND CEMENT CO.
CEMENT, TEXAS

AN ADAPTED WILEY EXTRACTOR FOR RUBBER EXTRACTIONS

By CHARLES P. FOX
Received March 22, 1913

The ordinary Soxhlet extractor is too small for acetone extractions when large quantities of rubber are desired. The Proctor extractor used in tannin extractions is also not satisfactory for rubber work. For charges up to 250 grams, a modified or adapted Wiley extractor has been used for several years and has given satisfactory results. This apparatus consists of the well-known Wiley metallic condenser, but in place of the original reservoir, a large (2 inches in diameter), long (18 inches), and strong glass tube with ground thick lipped top is substituted. The uniform diameter of the tube permits of large charges of thin sheeted rubber carefully rolled upon fabric being inserted into the tube, suspended from the condenser within range of the drip of the condensed and falling solvent.

To prevent a contamination of the purified rubber by accidental splashing of the resin solution, a disk of filter paper or cotton is inserted between the hanging charge and the solvent reservoir.

A metal spiral made of sheet tin is useful in preventing a superheating of the solvent and consequent foaming.

A steam bath may be utilized in furnishing the required heat for acetic and alcoholic extractions. Higher temperatures for nitrobenzene or kerosene work are obtained by direct flame carefully regulated, or by a paraffine bath.

395 DOYLE STREET
AKRON, OHIO

ADDRESSES

COMMENTS ON THE REPORT OF THE INVESTIGATION OF THE UNITED STATES PATENT OFFICE¹

By L. H. BAEKELAND
Received April 18, 1913

Whoever is interested in the patent situation of this country, should make it his duty to read the unusually interesting publication just issued by the U. S. Government, which covers 624 closely printed pages.

On August 21, 1912, the following joint resolution was passed: "That the President of the United States be, and he is hereby, Sixty-second Congress, 3d Session, House of Representatives, Document No. 1110. Report of the Investigation of the United States Patent Office, made by the President's Commission on Economy and Efficiency, Washington, December 9, 1912.

requested to cause the accountants and experts from official and private life now or hereafter employed in the inquiry into methods of transacting the public business of the Government in the several executive departments and other executive Government establishments, known as the Commission on Economy and Efficiency, to investigate fully and carefully the administration of the Patent Office with a view of determining whether or not the present methods, personnel, equipment, and building of said office are adequate for the performance of its functions, taking into consideration the present character and volume of business, and also such increase in complexity or volume as may reasonably be expected in the future, and to ascertain and recommend specifically to Congress not later than December 10,

1912, what changes in law, what increases in appropriations, and what additional building accommodations, may be necessary to enable the Patent Office to discharge its functions in a thoroughly efficient and economical manner, and to what extent any expenditures which may be recommended can be met by increases of Patent Office fees.

"All expense incurred in carrying out the purposes of this resolution shall be paid out of any funds in the Treasury of the United States not otherwise appropriated, and the sum necessary for said purposes is hereby appropriated: PROVIDED, That the total expense authorized by this resolution shall not exceed the sum of \$10,000."

The report, as presented, is signed by Frederick A. Cleveland, Walter W. Warwick, and Merritt O. Chance, Commissioners on Economy and Efficiency.

This interesting report enters into the many ramifications of our patent system, shows up its defects and indicates in a practical way possible methods of improvement.

An enormous amount of precise information has been collected by the above-mentioned commission, but what is more impressive is that all this has been accomplished with the expenditure of such a comparatively small sum of money as \$10,000, and the report should have been prepared and published three months and a half after the resolution was approved. This in itself is a worthy example of "economy and efficiency."

With these data at hand, in addition to the report of the hearings on the Oldfield Bill (see report No. 1161, to accompany H. R. 23,417, by Hon. W. A. Oldfield, House of Representatives, 62nd Congress, 2d Session), any future commission for the revision of our patent system will have its work much simplified.

Certain defects in the handling of the personnel of the patent office are pointed out; for instance, it is mentioned that there are no efficiency records for the examining force and that for many years there have been no examinations for the purpose of determining the efficiency of examiners and regulating their promotions and reductions. Such efficiency records, in conjunction with an examination system, would tend to encourage all employees to do their best work and would make adequate salaries a real and lasting benefit to the service.

Emphatic stress is laid on the unsuitability of the present Patent Office.

"In the preliminary survey preceding the investigation the commission was impressed with the idea that the building accommodations for the Patent Office are so inadequate as to render extremely difficult any substantial improvement in the work of the office. This impression has been changed as a result of the investigation until it has become a settled conviction that any permanent improvement in the quantity and quality of work done by the office, if done at a reasonable cost, must wait, upon provision being made for adequate office accommodations for the force of more than 900 people employed in the Patent Office."

It is a hopeful sign that the Bulkley Bill (H. R. 28,193, 62d Congress, 3d Session) should already have taken up this matter, and intends to provide a \$4,000,000 fireproof building. It is questionable, however, whether this sum of money will be sufficient for the purpose. When we take in consideration that the Patent Office has now an accumulated surplus of \$7,000,000 over all its expenses, there is no reason why this surplus should not be used for providing a suitable building, and the equipment that goes with it.

Through the courtesy of the authorities of the German Patent Office, I have recently been enabled to inspect that magnificent patent office building in Berlin, and its operation. I have been more than ever impressed with the fact how antiquated and inadequate our Washington Patent Office equipment has become in view of the enormously increased development of our country.

As to the needed changes in our patent laws, the remark is made that the present law is substantially the same as the act of 1836. There is a significant allusion to the conservativeness of lawyers and their opposition against any changes in procedure.

"No change, however much it may be needed to keep pace with changed conditions, can be made without vigorous opposition due to a large extent to that inherent prejudice against disturbing the daily routine life and the inconvenience of adapting one's mind to a new course of action. . . . Recommendations made by the present Commissioner of Patents for the amendment of laws to effect what he considers are improvements in the methods of the office and to expedite its work, are opposed by those who do not agree with him as to the wisdom of the changes as well as by those whose financial interests would be affected unfavorably. . . . the commission is convinced that any proposed change in the patent law and almost any proposed change in the methods of procedure in the Patent Office, will arouse opposition from some persons interested in securing patents."

This statement is very well corroborated by the answers to the list of questions sent out by the Economy Commission to members of the bar, inventors and others interested in matters before the Patent Office. More than 400 replies were received. On most questions there was a considerable divergency of opinion.

But even here it is significant that on question No. 24, relative to the desirability of creating one single Court of Patent Appeals, the answers were practically all affirmative and only a few opposed.

Questions 1, 2, and 3 asking opinions as to the advisability of abolishing one of the two appeals in the office and creating one appeal board of five or six members were answered in the affirmative in about 80 per cent of the replies. The direct negative to these questions was less than 20 per cent. The trend of the opinions expressed lies decidedly toward a single appeal to a board in the office, particular stress being laid on the importance of having the work of the primary examiner performed in a thorough and capable manner. The great majority of answers opposed the sitting of the commissioner, the assistant commissioners, or any administrative officer on this board, the idea being expressed that the commissioner should be left free to devote his time to purely administrative duties.

Answering question No. 14 "to what extent should the decision on such appeal operate as a final adjudication of patentability," a small number answered that the decision should be final, and a few that it should not be final. Some favored it being final only as to adverse decisions. Other suggestions were: It should be final, but not as against newly discovered prior art, in case of litigation under the patent; decision of the Patent Office in interference cases to be final and only to be opened in court upon new evidence found, as the proceedings are far less expensive in the office than in the courts.

Chapter 4 is devoted entirely to an examination of our cumbersome and time-robbing system of interference. The commissioners conclude that it would be better not to make any important changes in our present interference procedure. They seem to overlook the fact that our interference system, as it stands to-day, hardly protects the "first" inventor if the latter does not possess the abundant cash required to defend his rights against wealthy opponents. Furthermore, a good patent system should be devised in the interest of the nation, the public at large, and not for the limited individual benefit of some inventor or another.

The essence of good patent law is to induce inventors to disclose their invention as promptly as possible, so that the public may have the early benefit of such publication. Our interference proceedings, in conjunction with other defects in our methods

of allowing patents, encourage systematic delay in the publication of patents; in reality, a premium is now put on such delays.

All this would be much simpler if in all interference cases priority were allowed to the independent inventor who has filed his patent first, provided he has not copied nor stolen the invention from others.

The German law allows an almost absolute claim to priority to the earlier applicant. This system, therefore, has the great advantage of simplicity over the system in practice in the United States, but it may become a source of injustice in case the later applicant is really the earlier inventor. However, the later applicant has only himself to blame if he does not file his application in due time, instead of doing as is now the case, purposely postponing the filing of his claims under the immunity of our interference rules. This finally comes down to the question whether it is better to confer the right of priority to the earlier date of application which can clearly and instantly be established, or to the date of conceiving the invention and reducing it to practice, which brings forth all the uncertainties, vagueness, which frequently make our interference proceedings so absurdly long, complicated and expensive. Our present interference rules are undeniably a great handicap to the inventor of limited means; and our system is detrimental to the best interests of the nation. Indeed, it delays the essential benefit of publication of the invention; furthermore, in some cases it becomes a positive danger to any industrial enterprise when nobody knows whether he is infringing some unpublished patent rights which have been silently ripening to interference proceedings, protected by all the possible customary delays sanctioned by our rules of practice.

The German and British systems permit the filing of opposition proceedings within a certain period after a patent is allowed; this is an excellent simplified substitute for our interference proceedings. Members of the German patent office have invariably declared that they attach considerable importance to the maintenance of this system, because it tends to reduce the responsibility of the examiners and to enhance public confidence in the integrity and capability of the board of examiners; this in itself checks criticism to which such sensitive men as inventors are only too prone after they have encountered some disappointments in the office. I have noticed the same uniformly favorable opinion among German inventors, as well as patent attorneys and manufacturers, as to the advantages of the so-called opposition proceedings. Many of them, however, are of the belief that the British system, (which allows opposition to a patent during a certain period after the latter has been printed and published) is, however, more practical and expedient than the German method where opposition has to be filed before the patent has been printed, and before copies are readily obtainable except by means of special copies made from the pending application at the patent office.

As another check to worthless patents, the German law provides a safeguard in the method of annulment proceedings. Such proceedings are quite distinct and independent from any infringement proceedings. Any person, whether sued for infringement or not, may apply to the patent office for the annulment of any patent if he can prove that at the time of application the subject matter was publicly known, or was claimed in a prior patent, or was illegally appropriated by the patentee. However, in the latter case, annulment proceedings can be instituted only by the person from whom the invention was appropriated.

In a similar manner, a person who believes he can prove that he is prior inventor of an invention patented to another, and that the patentee has stolen his invention, can sue the patentee for an assignment of the patent to him.

There is still another safeguard in the German law, called the right of prior use (*Vorbenutzungsrecht*) which prevents the dangerous possibility which now exists in the United States, that a

business enterprise, started in good faith, might be held up at any time on account of a long secretly pending patent application.

In Germany, any person who, at the date of application of a patent, has already used the invention in that country, or made the necessary preparations for such use, has the right to use the invention for the requirements of his own business in his own works; but this right can only be transferred to others together with the good-will of the business.

It should be noted here that sometimes the suggestion has been made to cut down entirely our examination system, as well as our interference system, and to come back to a plain registration system, which was abandoned in this country 76 years ago, but is now known as the French system. The report of the commission says emphatically:

"To return to such a system would be a backward step."

"While there are some persons interested in the subject who believe that the United States should return to the system of registering patents and allow all questions of validity and priority of invention to be determined in the courts, these persons are decidedly in the minority."

In France, a patent may exist for years before an examination is made as to priority and patentability, because such a scrutiny only takes place in case of a patent suit; and even then, the examination is not made by technical experts but by the ordinary courts, who may or may not decide to hear experts. This absurd system accounts for the scant esteem with which patents are treated in the Latin countries where the French system is in use. The French system has certainly not shown the stimulating effect to invention and enterprise which the American system has introduced in such nations like Germany, England and the Scandinavian countries, which have adopted it in a more or less modified form.

It should be mentioned, furthermore, that in all countries where the French system is used, a patent really begins to be looked upon as serious after the corresponding German patent has been issued. This in itself, is the best tribute to the practical value of the preliminary examination system.

The most striking incongruity in our American system is that after a patent has been granted by a technical board, in infringement cases, this same patent is reexamined as to validity and patentability by a non-technical judge, in a non-technical court. This is the main reason why our system has been defined as "best in the world for lawyers and worst for inventors." (H. W. Leonard, *Electrical World*, 51, 1055.)

In this relation, the following words are very significant:

"The commission has been unable to see the benefit of the present system by which every question relating to a patent can be litigated in any part of the country.

"When the Patent Office shall have been furnished with adequate quarters and equipment and the most efficient personnel, it will be time to consider to what extent the decision of this office ought to be final in patent matters. When that time comes, it may be found advisable to consider whether a patent should not be made valid by law to the extent of giving the patentee a right to an injunction in a case against alleged infringers.

"This would probably require the adoption of the practice of publishing applications when ready for allowance, with the opportunity for anyone to file opposition within a limited time, and if none were filed or it was decided that the patent should be issued, it ought to be held valid for all purposes until declared invalid by court. Such a system would probably require also that any person claiming to be injured by the grant of a patent could file annulment proceedings within a limited period....

"There is a general complaint, although the commission is not advised as to the facts of the matter, that a grant of a patent is of no value to an inventor if it is in the interest of any person or corporation of financial strength to infringe it. The results after a patentee wins an infringement suit are often not of real

benefit to him, for, if he survives the suit, the actual recovery of adequate damages is exceptional.

"It would seem that the remedy for many of the difficulties of the present situation regarding patents will be found in the development of the Patent Office as an administrative court in which all questions relating to patents, excepting the question of infringement, will be finally decided, subject only to a review by an appeal to a court of patent appeals, with possibly a provision for certain questions going to the Supreme Court. Giving such jurisdiction to the Patent Office, and to one court, will tend to the development of a system of patent law that will be a benefit to the public and a protection to real inventors."

Chapters 5 and 6 are devoted to the classification division and to the scientific library and the search room. They point out the existing defects and contain many excellent suggestions.

The fact that in the files of the patent office, there are still missing copies of 60,000 German patents and of 6,000 French patents, is significant. It is true that for a certain period, France discontinued publishing its patents.

Several other countries, for instance, Canada and Belgium, do not publish their patents, excepting by title. Yet copies of every one of the patents published in those countries ought to be available in our search room; indeed, many of these patents contain important disclosures which have a direct bearing on the validity of the patents issued by the U. S. Patent Office.

It would not involve an exorbitant expense to have type-written copies made of the patents filed by those countries. A more satisfactory method would be to compel all countries, which belong to the International Union, to print every patent issued by them. This subject should be taken up at the next meeting of the International Convention, and could hardly cause any opposition, since almost all countries belonging to the convention already print these patents.

A very detailed criticism of the totally inadequate conditions of the building and the equipment of the patent office is made, and specific recommendations are offered for remedying this intolerable condition.

The commission overlooks the fact that the equipment of a new patent office will never be complete unless provision be made for a chemical, a physical and a mechanical laboratory, where simple direct tests can be made under the supervision of two or three experts—a chemist, a physicist, and an engineer; so that many simple questions which now baffle the examiners in their decisions on patentability could easily and quickly be decided by a direct test. Such a laboratory exists in the German Patent Office building.

The report is accompanied by several appendices, all of which make interesting reading. These appendices are as follows:

- A. History of the United States patent system.
- B. United States laws and rules of practice relating to patents, trade-marks, and prints and labels.
- C. The German patent law.
- D. The English patent law.
- E. Discussion of the German patent law and patent procedure.
- F. A comparison of the patent laws and procedure in Germany, England and the United States.
- G. Methods of examining applications.
- H. Publications of the patent office.
- I. Statement of the business of the patent office.
- J. Bibliography of the United States Patent Office.
- K. Classification of patents and printed publications.

Specialty instructive are appendices E and F, written expressly by Prof. Dr. Albert Osterrieth and Mr. A. du Bois-Reymond, both of Berlin, and leading authorities on the subject. The latter paper not only compares the advantages of the laws of Germany, England and the United States, but points out their relative defects which experience has proved to exist and, furthermore, discusses the differences in procedure in these countries.

This discussion of the advantages and defects of the leading patent systems of the world is a most valuable contribution and will be very useful in the consideration of changes that are suggested in the law and procedure of the patent system of the United States.

It is specially interesting to read the comments on the practical value of the so-called compulsory working clause or compulsory license clause in Germany and England, in view of the fact that an attempt is being made by the Oldfield Bill, and other proposed measures, to introduce this innovation in the United States.

In Germany, the compulsory working of patents has practically been abandoned and is merely kept up as a club to compel some countries like England, France and others into reciprocity treaties waiving the compulsory working of patents.

To the credit of the present commissioner of patents, it should be mentioned that he has already negotiated a treaty to that effect with Germany.

The United States, in accord with Germany, might have a decisive influence in abolishing this compulsory working clause in foreign countries, so irksome to American patentees, by passing a law whereby foreigners are compelled to work their patents in the United States, unless their country waives compulsory working of patents issued to American inventors.

The first Oldfield Bill had a clause of this kind, but it was so erroneously worded that in some paradoxical way, it gave superior advantages to foreigners over American inventors.

As to the compulsory working and compulsory license in Germany, we might best quote Prof. Osterrieth:

"In fact, very few patents have been revoked in Germany for non-working (one patent out of more than 2000). On the other hand, the working clause always threatens the patentee, hanging over his head like the sword of Damocles, as a great expert in patent matters once said. Besides, experience has shown that petitions for revocation are mostly entered by patent infringers, using the working clause as a defense.

"This explains why in the last 15 years, there has been a very strong movement in Germany for abolishing the working clause. This first induced the German Government to abolish the obligation of working by international treaties in the relations with Italy, Switzerland and with the United States. And finally the old working clause of the first patent law was abolished by the law of June 6, 1911.

"Since this law came into force, *i. e.*, July, 1911, no obligation of working a patent exists in Germany. No patent can be revoked on the ground that it is not being worked. Yet, considering the legislation of some countries which threaten foreign patentees with revocation of these patents, if the invention is exclusively or mainly manufactured abroad, the German Government resolved to provide for a similar clause, applicable at least against such countries where German manufacturers have to suffer from such legislation.

"It has therefore been stated in the above mentioned law of 1911, that a patent can be revoked, as far as international treaties do not provide to the contrary, if the invention is exclusively or mainly manufactured or carried out outside the German Empire, and its possessions. This clause does evidently not apply to citizens of the United States, even if an American has acquired a German patent from a patentee belonging to another country. Yet this might lead to abuses. Therefore, there has been provided a complementary clause, saying that transferring a patent to another person is ineffective if this transfer has been made only with the intention of avoiding revocation.

"According to the former German law a patent could be revoked, after expiration of three years from the date of granting, *if it appeared in the public interest* that permission to use the invention be granted to others but the patentee refused to give such permission in return for adequate remuneration with adequate

security. This clause has proved most ineffective as *no single case of revocation of a patent on this ground has been known*. Therefore, when the abolition of the working clause was discussed, it was suggested to do away also with that clause on the obligation of granting licenses. It was objected that cases might happen where the use of a patented invention by others than the patentee could be necessary for the *public welfare*, for instance, manufacturing certain drugs in case of an epidemic."

This consideration seemed to justify the insertion of the following clause in that new law of 1911:

"If the patentee refuses to grant license to another for using the invention upon the offer of an adequate compensation and security, such grant for using the invention can be allowed (compulsory license), if such granting seems necessary in the public interest. The grant may be limited or subject to special conditions."

This detailed report of the Commission on Economy and Efficiency is supplemented by some specific recommendations as follows:

I. That a new building specially designed, equipped, and furnished be constructed on a suitable site in the city of Washington, for the exclusive use of the United States Patent Office.

II. That the number of officers and employees of the United States Patent Office be increased, and the increases and readjustments of salaries be made as shown in detail in this report involving an increase of 36 in the number of employees and a total increase of \$236,550 in the pay roll.

III. That the Commissioner of Patents be the head of the Patent Office; that his duties be the same as are now prescribed by law, excepting that he be relieved from the consideration of cases on appeal; that he be aided by an assistant commissioner and seven supervising examiners in the administrative work, including control of the methods and procedure of the 43 examining divisions in the allowance and rejection of applications for patents.

IV. That one appeal within the United States Patent Office be eliminated; that the number of members of the board of examiners in chief of the Patent Office be increased from three to five; that all appeals within the office be taken to that board; that its decision be the decision of the Patent Office; that the appeal therefrom be to the Court of Appeals of the District of Columbia, as now allowed from the decisions of the Commissioner of Patents.

V. That the fee for filing an application be increased from \$15 to \$20; that appeal fees be adjusted to the conditions arising from the elimination of one appeal; that a fee of 25 cents be charged for each additional patent, etc., included in one instrument presented for record; that all fees be paid directly to the Patent Office; that refundment of fees paid by mistake be made by the financial clerk and not by warrant from the Treasurer.

VI. That the life of a patent be so limited as to expire 19 years from the date of filing the application therefor, excluding the time (not exceeding two years) during which an application may be involved in interference.

VII. That the work of reclassifying patents and digesting of printed publications, and providing facilities* for simplifying and making more accurate the search, be recognized by an appropriation for an adequate force to be employed upon such work.

VIII. That the subscription price of the Official Gazette be increased from \$5.00 to \$10.00 and the method of distribution to libraries be changed to reduce the number of copies so distributed.

IX. That all the work of producing the publications of the Patent Office, including copies of patents, be done at the Government Printing Office.

X. That an appropriation be made for the repair of the rooms occupied by the Patent Office and for the installation of suitable lighting and ventilating facilities and for the purchase of new furniture and equipment.

YONKERS, N. Y.

THE PLASTICITY OF CLAY¹

BY JOHN STEWART

It is one of the peculiarities of human endeavor that action taken for a certain purpose often results in the accomplishment of an entirely different and unexpected result. *A priori* it would hardly be expected that a study of the organic phosphorus of the soil would have any bearing on the plasticity of clay, but such is the infinite inter-ramification of the facts of nature that they lead to strange results.

So far as the writer is aware, no satisfactory explanation of the cause of the plasticity of clay has ever been advanced. Numerous attempts to explain the phenomenon have been made, but none of the results has met with general acceptance. Hilgard² reviewed some of the most important of these attempts, but indicated by his treatment of the subject that the question was still an open one. Hopkins³ mentions plasticity as a *property of clay*. Thorp,⁴ in his exposition of the chemistry of the ceramic industries, offers no explanation of the cause of the plasticity of clay, although without this property the industry could not exist. Ashley⁵ reviewed the literature of colloids and of clay, and made a study of the absorptive power of some clays for certain dyes. His work was based on the idea that "clay is . . . a mixture of granular matter and a colloid gel," and had for its purpose the development of a method of measuring the plasticity of clay by utilizing the absorptive power of colloids for this purpose. In a later publication, Ashley⁶ discusses plasticity of clay on the same general lines. He says: "The colloid matter of clays may be considered as consisting of complex mineral and organic acids and salts." Bleining⁷ studied the effects of heating clays to temperatures under 400°. He found that the plasticity was decreased and that there was *not* a corresponding change in the absorptive powers of the clay. Acheson,⁸ in 1901, ground clay in a water extract of straw and found that this treatment increased the plasticity. He considered this result to be due to the *organic* matter in the water extract. In 1904 this result was claimed to be due to gallo-tannic acid, and seems⁹ to have been regarded as a *physical* and not a chemical action. Thus the importance of Acheson's observation does not seem to have been recognized by investigators. P. Rohland¹⁰ attributed the plasticity of clay to hydroxides of Si, Al, and Fe. He noted that fuller's earth *absorbs* unsaturated *hydrocarbons*, and he recommended the use of clay to purify factory wastes.

There are some facts relating to the plasticity of clay which have received general recognition and acceptance as being true. First, *pure* clay is *not* plastic. Hilgard¹¹ says: " . . . it is readily mistaken for chalk (and is sometimes used as such), being powdery to the touch and entirely devoid of plasticity " Those engaged in the ceramic industries call the purer clays "lean" on account of their lack of plasticity. Second, *impure* clays are the plastic ones. These are the "fat" clays, so-called by those engaged in the ceramic industries because of their possession of plasticity. Third, it is a common practice in the ceramic industries to mine the clay and allow it to *weather*¹² for months before use. This is said to increase the plasticity. Fourth, *ignition* destroys the plasticity of clay. Attempts to

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

² "Soils," 1906, pp. 57-62.

³ Hopkins, "Soil Fertility and Permanent Agriculture," p. 88.

⁴ "Outlines of Industrial Chemistry," 1909, pp. 191-200.

⁵ U. S. G. S., *Bull.* 388 (1909).

⁶ C. A., 5, 1748 (1911).

⁷ *Ibid.*, 6, 175 (1911).

⁸ "Some Chemical Problems of To-day," R. K. Duncan, 1911, pp. 118-119.

⁹ U. S. G. S., *Bull.* 388, 12 (1909).

¹⁰ C. A., 4, 803, and other abstracts.

¹¹ "Soils," 1906, p. 59.

¹² Thorp, "Outlines of Industrial Chemistry," 1909, 194. Roscoe and Schorlemmer, "Treatise on Chemistry," (1) 2, 495 (1883), new edition.

all failed. Fifth, a pure clay is a hydrated *aluminum* silicate.

Two other facts¹ which are not as generally recognized as the above may be mentioned here. First, Ries in his work on Michigan clays found examples of lean clays absorbing a greater percentage of water than fat clays absorbed. Second, Grout found that a shale increased largely in plasticity on weathering, but that the combined water remained practically constant. It is also a fact that shale loses its plasticity on being metamorphosed into slate.

During the past year the writer made an observation which is of considerable importance with reference to this subject of plasticity. The observation referred to was made during a study of humus and the organic phosphorus of the soil, in which the writer was engaged during the summer of 1911. This study resulted in some interesting data and conclusions with reference to the organic phosphorus, iron and aluminum compounds of the soil. A paper has been prepared embodying the data and conclusions resulting from the work and not embodied in the present article.

In the study of humus, or the constituents of humus, there is a fundamental difficulty, due to the deflocculation of the clay by the alkali used, which makes it almost impossible to obtain a humus solution free from suspended clay. In searching for a means of overcoming this difficulty the writer added a small quantity of alumina cream, washed free from salts, to a humus solution containing some suspended clay, and filtered the liquid. A perfectly clear humus solution passed through the filter; but the residue on the filter was dark colored, indicating that chemical action had occurred between the humus and the alumina cream. This indicated that this method could not be used for quantitative work, and, consequently, the filtered solution and residue were set aside for several days. The filtered solution was then placed in an evaporating dish to determine if the chemical action of the alumina on the humus had seriously interfered with quantitative results. After being on the water bath a short time a flaky, dark brownish colored solid separated out, leaving the humus solution almost colorless. This solid was gelatinous, and some of it floated on the liquid. As the solution evaporated, these flakes adhered to the sides of the evaporating dish and to the glass stirring rod, sticking almost like glue. The solid was then filtered off and leached with one per cent hydrochloric acid. It proved to be rather difficult to decompose. The acid was used cold at first, then hot acid was tried; and a hot stronger acid was used before a very complete decomposition of the precipitate was obtained. The acid solution gave a heavy precipitate of *aluminum* hydroxide on adding ammonia. There was a residue of organic matter left on the filter which dissolved readily in ammonium hydroxide.

Now taking all these facts into consideration, the writer suggests that the plasticity of clay is due to the presence of an *organic aluminum* compound (or compounds). This will satisfactorily explain all the important, established facts concerning the plasticity of clay. This explains why it is the *impure* and not the *pure* clays which are plastic. This explains why *ignition* destroys plasticity and why levigation fails to restore plasticity to the ignited clay. This explains the heretofore unexplained practice of weathering clay before using it in the ceramic industries. In 1883, Roscoe² and Schorlemmer said: "It . . . is allowed to remain for a considerable length of time in a moist place, when the organic matter contained in the clay undergoes putrefactive decomposition: this seems to increase the plasticity of the mass, but the exact action which takes place under these circumstances is not well understood." This explains why shales lose their plasticity on being metamorphosed into slate. This explains the observations of P. Rohland, mentioned by Ashley,³ to the effect that plasticity

of clay is reduced by all bases and all salts of strong bases with weak acids which hydrolytically split off hydroxyl ions and that neutral salts have no effect on the plasticity; for, the *aluminum* organic compound observed by the writer is soluble in alkali. This gives a partial explanation of the universal observation that hydrous *aluminum* silicates are sometimes plastic, while similar hydrous silicates of other bases, as serpentine, are not plastic; and, taken in connection with some other facts which readily suggest themselves, makes a complete explanation of the observations.

In all probability, the writer's observation gives at least a partial explanation of the use of fuller's earth for purifying mineral and vegetable oils. The writer suggests also that the heretofore unexplained fact that vegetable oils purified in this way generally have a bitter taste, is due to the formation of an *aluminum* organic compound which is somewhat soluble in the oil, and to which the bitter taste is due.

It is interesting to recall in this connection an observation made by Th. Schloesing¹ in 1874. After washing a kaolin with dilute acid, he separated it into several fractions by mechanical analysis, using ammoniacal water. Out of five fractions, only one showed any marked plasticity. This was the fraction that was still in suspension after 27 days. Schloesing called this fraction "colloidal clay;" and it was so plastic as to be sticky and adhered strongly to the porcelain dish in which it was dried. In the light of the writer's observation, and considering Schloesing's method of work, it is evident that Schloesing's "colloidal clay" contained a large proportion of an *organic aluminum* compound (or compounds) to which its plastic, sticky properties were due.

In speaking of "colloidal clay," Hilgard² said: "(It) . . . bears more resemblance to glue than to the clay of every-day life. Like glue, too, the dried colloidal clay adheres to the tongue. . . . it assumes a highly plastic and adhesive condition, so that it is difficult to handle and almost as sure to soil the operator's hands as so much pitch." Hilgard³ also says: ". . . the several humates (of lime, magnesia, iron), which, when fresh, are colloidal (jelly like) like clay itself, but unlike the latter, when once dried do not resume their plastic form by wetting (Schloesing)." No mention of *aluminum* humates was made by Hilgard in this connection. His treatment of the subject also indicates that up to the time of his writing there had been no suggestion of a possible causal relationship between the plasticity of humates and the plasticity of clay. On the contrary, Hilgard⁴ states: "A similar process," (*viz.*, to that of Johnson and Blake,⁵ who levigated kaolinite in a mortar for a long time in an attempt to produce plasticity) "but continued much longer by the mechanical agencies concerned in soil formation (see Chap. 1), is unquestionably the chief factor⁶ concerned in the formation of natural plastic clays; but whether this is the *only* process by which powdery kaolinite may be transformed into plastic clay is a question not definitely settled."

In view of the observations of the writer and of Schloesing, it is evident that if plastic clays be subjected to treatment for the removal of the humus they will lose their plasticity. These observations point the way for the development of analytical methods for estimating the plasticity of clay; and also point the way for methods of treating clays which are too "lean" (or too "fat") for certain uses in the ceramic industries. Further research along these lines might prove very interesting and also of considerable practical value. It should probably be mentioned in this connection that Ashley⁷ has already indicated

¹ *Compt. rend.*, **79**, 376-380, 473-477 (1874).

² "Soils," **1906**, pp. 61 and 62.

³ "Soils," **1906**, p. 110.

⁴ "Soils," **1906**, p. 60.

⁵ *Am. Jour. Sci.*, [2] **43**, 357.

⁶ These italics are Stewart's.

⁷ *C. A.*, **5**, 174-175 (1911).

¹ U. S. G. S., *Bull.* **388**, 28 (1909).

² *Treatise on Chemistry*, [1] **2**, 495 (1883), new edition.

³ U. S. G. S., *Bull.* **388**, 21 (1909).

some means of improving clays in accordance with these principles; but Ashley's work, in this connection, appears to be based upon the observations of Rohland,¹ for which neither of them apparently had a satisfactory explanation.

While the writer does not doubt that time will prove his explanation of the plasticity of clay to be correct and that these aluminum organic compounds are the only important ones concerned in this phenomenon—he would not be understood as claiming that in some cases other compounds may not contribute to the plasticity of *very impure* clays in a very minor degree. In this connection he would call attention to the fact that the "lime muds" obtained in purifying sugar beet juices are

very plastic. These are composed of granular calcium carbonate and coagulated albuminous substances and *calcium organic* compounds mainly. Limestone is generally impure and there may be also magnesium, iron and aluminum organic compounds in the "lime muds." There can be no doubt that plasticity results from the mixture of a granular substance and a gelatinous substance in due proportion. There are many granular substances and many gelatinous substances; and so the plasticity of different substances is due to different components of the mixtures.

UTAH EXPERIMENT STATION
LOGAN, UTAH

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE TINNING INDUSTRY

The tinning industry from a chemical standpoint is discussed by Hodgson in *The Chemical World*, 2, No. 3, 98. At first tinning was practiced as an auxiliary branch of various handicrafts, such as that of the copper-smith, spur-maker, etc., but its rapid development effected its separation as an individual industry. As early as 1670, an English company was organized to start a tin-plate works at Pontypool, but patent difficulties occasioned their stoppage. In 1720, however, works were started once more at Pontypool, and being followed by others in South Wales, the industry developed so extensively as to become probably the most important seat of this manufacture in the world.

The pickling process has exercised the minds of those engaged in the industry from its inception, and the problems it presents are essentially of a chemical character. The real development of tinning, therefore, runs parallel with that of the production of mineral acids and sheet steel. Pickling was originally performed with organic acids, and Reaumur was the first to recommend dilute sulfuric acid for pickling sheet iron. At the present time, the sheets are very carefully dipped into a mixture of dilute sulfuric and hydrochloric acids, then well washed, dried, and gradually heated to a cherry-red heat in iron boxes placed in furnaces. After remaining several hours in the furnace, the sheets are slowly cooled and smoothed between hard rollers, again rapidly heated with exclusion of air, and dipped into a fermenting mixture of bran and water. A final immersion in dilute sulfuric acid, with subsequent washing and sand scouring, causes the sheets to be ready for the plating process. (This is the Welsh practice, and, while it has been found to be satisfactory, shortly before the development of the tinplate industry in the United States, there were introduced various improvements, principally mechanical, to reduce the labor involved, to cheapen the cost of manufacture, and to lessen the consumption of raw materials. On these points, see W. C. Cronmeyer, German Engineers' Society, Pittsburgh, 1899.—W. A. H.) In the United Kingdom, until government action was taken, lead was added to the fused tin for easier and cheaper tinning, and Newton proposed the addition of bismuth. The usual tinning plant, or stow, consists of five vats: the first and fifth, the "grease-pots," contain tallow or palm oil; the second, the "tinman's pot," is filled with molten tin at 400° C., this being covered with a layer of palm oil to prevent oxidation. The sheets are placed in the grease pot while wet and after 10 minutes are taken to the tinman's pot. Small metallic objects are, however, usually tinned by the blanching process. The well-scrubbed object is placed for several hours in a boiling solution containing tin or alkali stannates, and is then washed with water, rubbed and dried. Electro-tinning has recently made important progress, although as yet no marked commercial success has been attained. A beginning has been

made at Swansea to coat black plates with aluminum by a cold wet electric process.

Among the ideas Thomas (*Chem. Trade J.*, 52, 341) considers worthy of investigation are the following:

- (1) Over and under black pickling, the influence of strength and temperature of the acid solution, and of time.
- (2) Effect of varying temperatures and time of annealing.
- (3) Light and heavy cold rolling.
- (4) Temperature effects in the tinning operations.
- (5) Differences from the tinplate trade point of view between acid Bessemer steel, basic Bessemer steel, acid open-hearth steel, and basic open-hearth steel, and the comparative tin consumption of each kind.

LINSEED OIL

The distribution of the world's linseed shipments has been as follows (*Chem. and Drug.*, 1913, Jan. 25):

Year	Distribution, in tons		
	World's seed shipments, in tons	United Kingdom	The Continent and the United States
1903	1,178,150	385,954	592,196
1904	1,523,426	505,519	1,017,907
1905	1,110,773	345,412	795,361
1906	1,080,883	286,140	794,743
1907	1,368,311	372,537	995,774
1908	1,432,186	382,169	1,050,017
1909	1,293,836	303,237	990,599
1910	1,153,923	236,066	917,857
1911	1,101,690	243,338	858,352
1912	1,127,424	257,294	870,130

The production of linseed for the last ten years is reported as follows in tons:

Year	Argentina	India	U. S. A.	Canada	Russia
1903	937,601	481,367	682,513	21,100	461,314
1904	740,000	571,832	888,013	13,388	471,836
1905	591,912	347,400	711,944	18,342	421,000
1906	825,764	383,400	626,800	25,888	540,500
1907	110,710	425,200	646,228	13,401	550,590
1908	1,048,852	163,200	648,128	19,133	500,339
1909	716,515	297,700	487,817	120,829	558,360
1910	595,000	527,600	317,950	100,974	680,000
1911	572,000	563,600	484,280	196,675	670,000
1912	1,130,000	641,200	701,828	528,505	680,000

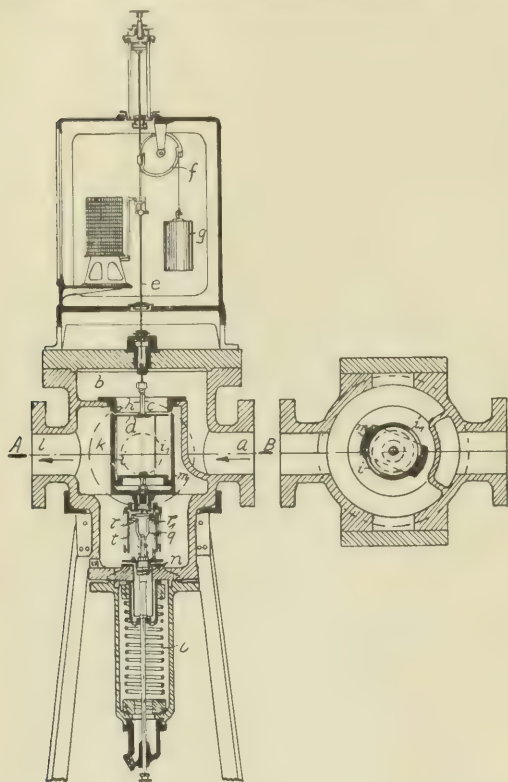
Practically the whole of the Argentine exportable surplus will be diverted to Europe, as well as the great bulk of the Indian supplies and a considerable tonnage from Russia.

THE "RHENANIA" STEAM METER

A Dresden firm has placed upon the market a meter which is reported to successfully measure the whole quantity of steam

¹ U. S. G. S., *Bull.* 388, 21 (1909).

passing through it, without offering resistance to its passage. Small condensation losses and leakages, accurate to 3 per cent, are indicated directly, it is not affected by water or shock; and direct readings of the actual steam consumption in kilogram hours may be made, independent of pressure. The meters are fitted into the steam circuits by means of adapters.



The construction of the "Rhenania" meter is shown herewith. Its operation is based upon the formula $G = F \cdot v \cdot y$, wherein G is the quantity of steam in kilograms, F is the size of the passage in centimeters (height, $h \times$ width, g), v is the speed of the steam in meters per second, and y is the weight of one cubic meter of steam in kilograms at the correct pressure. It may be used for superheated steam, in which case the temperature is recorded, and has been tested up to pressures of 12 atmospheres.

THE OFFICIAL TONNAGE REPORT OF THE STEEL CORPORATION FOR 1912

	Tons
Iron ore.....	26,428,449
Coke produced ..	16,719,387
Coal mined ..	5,905,153
Limestone quarried ..	6,124,541
Blast furnace production ..	14,186,164
Bessemer steel ingots produced ..	6,643,147
Open-hearth steel ingots produced.....	10,358,076
	17,001,223

According to the *Industrial World*, 1913, 345, the net income was \$77,075,217; the ordinary repairs and maintenance amounted to \$43,853,137; and the dividends to \$50,600,000. The number of employees were 221,025, and these received salaries and wages amounting to \$189,351,602, or \$856 per man for the year.

THE STATUS OF THE CHEMICAL INDUSTRY OF AUSTRIA-HUNGARY

Notwithstanding the fact that political disturbances caused a certain depression in industrial affairs, the chemical industry of Austria-Hungary did not suffer much during 1912, as shown by the following statistics (*Chem. Ztg.*, 37, No. 22, 23).

	METRIC TONS	
	Imports	Exports
Chemical products and crude materials.....	440,806	136,130
Varnishes, colors, medicinal preparations, and perfume materials.....	11,531	4,729
Waxes, soaps, etc.....	1,414	2,185
Salt.....	113,287	17,588
Sugar.....	6,004	699,676
Technical fats and fatty acids.....	64,310	57,948
Fats and oils.....	19,742	630
Coal, etc.....	12,995,858	8,667,808
Earths, ores, etc.....	973,869	178,551
Mineral oils, shale tar, etc.....	38,994	609,582
Gums and resins.....	103,434	41,393
Dyes and tanning materials.....	70,388	61,956

THE FOREIGN METAL TRADE OF THE UNITED STATES IN 1912

The Bureau of Foreign and Domestic Commerce, of the Department of Commerce and Labor, reports that the exports and imports of metals in the United States for the full year were as follows:

	Exports	Imports
Copper, long tons.....	357,423(a)	183,143
Tin, long tons.....	390	51,787
Lead, short tons.....	64,906(b)	83,560
Zinc, short tons.....	6,682	11,115
Zinc in ore, pounds.....	13,556,954(c)	39,995,719
Nickel, pounds.....	25,815,016	42,168,769
Antimony, pounds.....	50,984	17,645,870
Aluminum, pounds.....	211,036(d)	22,759,937
Platinum, ounces.....	(e)	104,683
Chrome ore, tons.....		53,929

(a) The exports of copper to various countries in 1912 were as follows in pounds: Germany, 252,156,012; Holland, 152,618,177; France, 152,618,177; Belgium, 131,362,694; Great Britain, 95,422,292; Italy, 47,251,432; and Canada, 30,302,856. A considerable part of the exports to Holland were intended for Germany.

The greater part of the copper imported as brought to be refined and put into marketable shape. It was imported principally from Mexico, Canada, Peru, Spain and Chile.

(b) Almost all the lead exported is foreign lead refined here.

(c) 34,128,163 pounds of zinc oxide and 410,568 pounds of dross were exported.

(d) The manufactures of aluminum were valued at \$1,347,021; the quantities were not given.

(e) In 1911, 181 ounces of platinum were exported and 122,390 ounces imported.

FURTHER INVESTIGATIONS FOR SECURING SOUND STEEL INGOTS

At the February 19th Meeting of the American Institute of Mining Engineers, P. H. Dudley reported that the following conclusions may be drawn for the manufacture of basic open-hearth steel rails:

(1) The chemical composition should provide for sound steel of ample physical properties of tenacity and toughness rather than hardness combined with brittleness.

(2) Phosphorus and sulfur should be of minor content so the bath of metal can be purified to produce the necessary toughness and ductility.

(3) The ingot should be of such shape and weight that under good mill-practice and suitable deoxidizers it can be made with controlled segregation and only a trace of a shrinkage-cavity in the top; then, when bloomed under its equalized initial heat, it is rendered pipeless by the usual 8-10 per cent discard.

(4) Aluminum can be wholly and silicon partly displaced

with advantage as deoxidizers by the use of ferro-titanium to purify, solidify, and check segregation.

(5) Ductility and elongation tests (see *Eng. Record*, September 21, 1912, 322) to date furnish the best and only prompt means of determining the degree of purity of the steel per melt as it is made by indicating the physical properties secured before another melt is tapped from the same furnace.

(6) Every process or step of the entire manufacture of the steel and rolling and finishing of the rails must contribute its part to secure the highest quality of the product incident to the chemical composition.

In the discussion of Dudley's paper a number of points of interest were brought out. There seemed to be an approximate uniformity of belief that the present method of cropping to get rid of pipes is satisfactory, and that an arbitrary percentage to be cropped would be undesirable and unfair to the manufacturers of the best steel. The general belief also appeared to be that the best steel was that so made that pipes formed, that special processes for eliminating pipes were likely to introduce greater danger of segregation, and that the essential requirement for minimizing pipe was to compel the ingot to cool slowly in a direction upward from the bottom.

THE "OPTIMUS PLASTIC ALLOY"

Tests made recently in France on bus-bar joints showed that on a bus-bar carrying 1760 amperes, 84.5 watts were lost per hour owing to heating. In a plant operating 10 hours per day and 300 days per year, *Power* observes, this would represent 253 kilowatt-hours per year. This loss may not appear large, but it should be noted that the joint tested was only one of a number of similar ones on the switchboard.

A preparation termed "Optimus Plastic Alloy" has been put on the market for reducing such losses. It is in the form of a metal putty which is a good conductor, and is applied in such a manner as to fill up the cavities on the surface, whereby, it is claimed, the plates are made continuous electrically, the above-mentioned loss is reduced by about 85 per cent and moisture is excluded. The application of the alloy is made in the cold.

"AJAX ANTI-RUST SHEETS"

A Philadelphia company is now marketing sheets consisting of a galvanized black plate, over which is placed a coating of lead. The iron is protected by the electro-positive zinc; the zinc by the chemically inert lead. In addition, it is claimed that the lead penetrates the zinc coating, making it less likely to scale off during bending, etc. The manufacturers recommend the plate for dye-works, smelters, and in other construction likely to be exposed to the action of destructive and corrosive fumes and gases.

THE PAINTING OF STEEL PASSENGER COACHES

The painting of steel passenger coaches with baking enamels has recently been found to be successfully and economically accomplishable, and a railroad operating between New York City and New Jersey points has used baking enamel in repainting its rolling stock with good results. This work is described in the *Electric Railway Journal*, 1913, Jan. 25. In this case, since the cars are used almost exclusively in tunnel service, the exterior appearance of the coaches was not considered but the interior finish was desired carefully done.

After cleaning, the car is first heated to 200° with electric heaters strung between the stanchions in the car. The temperature is controlled by a man who watches, through a window, a thermometer inside the car, the current being turned off or on as needed. Windows and doors are closed tight and ventilators are covered with newspapers stuck to the roof with tar. The car is allowed to remain at 200° for one hour to drive

off moisture and equalize surface expansion and contraction. The heat is then shut off, the car is cooled down to about 115° and the priming coat applied while the metal is hot. The temperature is again raised to 200° and the enamel baked for three hours. Second and third coats are baked at 140° for three hours, and the last coat for three hours at 130°. All coats except the first one are applied with the air in the car cooled to about 70°. The old enamel is scraped off by hand before painting to remove the bulk of the covering; the surface is then gone over with a standard varnish remover carefully applied so that all the old enamel is removed from the pores of the metal. To clean off traces of the varnish remover, the surface is rubbed with waste soaked in gasoline.

The costs are in general about equal to those of common high-grade painting. The best of materials have to be used, but a given volume of baking enamel covers about twice as much surface as the air-drying variety.



THE "DISSIPATOR"

The "Dissipator," the rights on which are controlled by a Frankfurt a/M, Germany, concern, and which is illustrated herewith, is reported to have been introduced into the industries with great success. It is said to render obnoxious gases less objectionable by diluting them with air and to "eliminate visible fumes at a short distance from the chimney." The manufacturers claim that the "Dissipator" can be erected by any competent chimney builder, that it can be fitted on to existing chimneys, and that there are no operating expenses.

RECOVERY OF COKE FROM ASHES

Power reports that the recovery of the combustible matter remaining in coal ashes is receiving earnest attention at present in Germany, where it is said 150 million tons of coal are burned annually and about one-third of that amount is burned in furnaces from which the ash and cinder would yield 6 to 8 million tons of residual matter containing 2 to 3 million tons of combustible matter. A mechanical process for separating the combustible matter from ordinary boiler ashes has been devised by A. F. Muller. This consists in first crushing the ashes and then separating the components thereof by placing the ashes in liquids of different specific gravities; the residual matter is said to be practically free from any combustible material, and may be used in the manufacture of concrete blocks. An experimental plant is reported to recover 38 tons of coke, 1/2 to 2 in. in size, from 2,000 tons of boiler ashes; this recovered material, when dry, contains about 84 per cent. combustible matter and possesses a calorific value of about 6,500 B. T. U. per pound.

THE PRODUCTION OF FLORIDA PHOSPHATE IN 1912

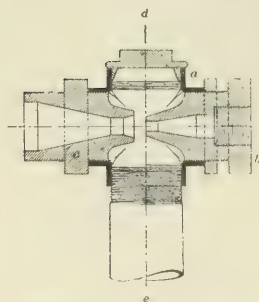
The State Geologist, E. H. Sellards, reports (*Eng. Min. J.*,

95, 992) that the production of phosphate rock in Florida for 1912 was 2,579,865 long tons, as compared with 2,494,572 tons in 1911. The production of hard rock in 1912 was 536,379 tons, as compared with 474,094 tons for the previous year. The output of pebble phosphate in 1912 was 2,043,486 tons as compared with 2,020,478 tons in 1911. Thirty companies in all were engaged in mining phosphate in Florida in 1912; of these, 14 mined hard-rock phosphate and 16 mined pebble phosphate. The foreign shipments during 1912 amounted to 1,203,005 tons, while 1,219,927 tons were consigned for domestic shipment. Hard-rock phosphate sold at the mines at about \$6.00 per ton, while pebble phosphate sold at the mines at \$2.75 to \$4.50 per ton, depending upon the grade.

THE PRODUCTION OF CYANAMIDE

FIRM	WORKS	20% Cyanamide in tons 1912	1913 (probable)
Société des Produits Azotés.....	Notre Dame de Briançon, Savoie, France	7,500	7,500
	Martigny, Valais, Switzerland	8,000	12,000
Bayerische Stickstoffwerke Aktien Gesellschaft für Stickstoff-dünger.....	Trostberg, Germany	15,000	15,000
	Westeregeln, Knapsack, Germany	15,000	45,000
Northwestern Cyanamide Co.....	Odda, Norway	24,000	52,000
	Alby, Sweden	15,000	15,000
	Meraker, Sweden		12,000
Stockholm Superphosphate.....	Johannesberg, Sweden		15,000
Stà. per la Fabricazione dei prodotti Azotati.....	Terni, Perouse, Italy	24,000	24,000
Société Piémontaise de Carbure de Calcium.....	St. Marcel Vallee d'Aoste, Italy	3,500	3,500
Stà. Sufid Société d'Utilisation des forces hydrauliques de la Dalmatie.....	Sebenice, Dalmatia	5,000	5,000
	Almissa, Dalmatia		
American Cyanamide Co.....	Niagara Falls, Ont.	24,000	24,000
	Alabama plant		24,000
Société Japonaise pour la Cyanamide.....	Osaka, Japan	12,000	12,000
Total production.....		153,000	260,000

THE "FITTING-INJECTOR DEA"



A Hannover-Linden, Germany, firm has placed on the market an injector which is said to perform the work of other types of injectors, while the parts may be replaced during operation. It is said to be particularly suitable for the transportation of liquids containing suspended particles and alkaline liquors; it is in use in Germany in plants for leaching sodium and barium sulfides.

The construction is shown in the accompanying figure. *a* is a cross-piece; *b* is the steam entry; *c* is a nozzle for pressure entry; *d* is a screw

plug for cleaning purposes; and *e* is a suction tube.

ELECTROLYSIS FROM STRAY ELECTRIC CURRENTS

The matter of electrolysis from stray electric currents is one of importance to the chemical, gas and municipal engineer, especially since Gardner (*J. Frank. Inst.*, 1908, 459) has shown, in an investigation of the effect of an electric current on the speed of the corrosion of steel plate, that in every case the action seemed to have been about doubled in its intensity by the passage of the current. The remedies brought out in a very recent paper by Ganz (*Am. Gas Light J.*, 98, No. 12, 190) are therefore pertinent, and accordingly his conclusions are given at some length.

Experience shows that where there is serious trouble from electrolysis caused by large stray currents leaking from street railways, the bulk of this trouble is due to defective rail bonding, to ground connections from the negative bus-bar, and to lack of return feeders to carry the current back from the rails to the power station. While stray currents can only be entirely eliminated by insulating the return circuit by the use of a double trolley, either overhead or in conduit, it is nevertheless a fact, not generally appreciated, that where large stray currents exist, due to the above-mentioned causes, these can always be reduced to a small fraction of their present value by removing all ground connections of the negative bus-bar, and installing insulated return feeders proportioned for equal drop from radially disposed points in the track system located at some distance from the power station. By this method, the rails are drained of current, and any desired part of the voltage drop can be removed from the rails and transferred to insulated conductors from which the currents can not leak. In Europe such radial insulated return feeders, for bringing the current back from the rails to the power station, are made necessary by regulations limiting the allowable drop in voltage in the rails; and, in most cases, such installation of insulated return feeders have substantially removed serious trouble from electrolysis. This system of minimizing stray currents by means of radially disposed insulated return feeders has also lately been installed in a number of American cities, and the method is becoming recognized by railway engineers as by far the best. This system removes the root of the trouble, by draining the rails of current and removing the voltage drop from the rails, and consequently prevents any substantial leakage of current through the ground; it is, therefore, correct in principle. The objection to such a method has been the expense of the system, but Ganz states that this is not the case. The fact is, he continues, that in many American railways there is practically no installation of negative feeders, and that railway companies are often unwilling to install even a moderate amount of return feeder copper. Ganz concludes by remarking that in order to effectively install and maintain an adequate return feeder system that will reduce stray currents on underground piping systems to reasonably small values, it is essential that pipe-owning companies co-operate with railroad companies by affording them access to their pipes for making the necessary measurements, etc.

STANDARDS FOR HYGIENIC PURITY OF PUBLIC WATER SUPPLIES

J. W. Ellms (*Eng. Record*, 67, No. 11, 293) suggests the appointment of delegates from each of the large engineering societies, waterworks and sanitary associations to formulate a plan of procedure for preparing standards of purity for public water supplies. It is proposed that these delegates work in conjunction with any state or federal committee.

Among the matters which should be discussed are the following:

(1) What diseases may be legitimately regarded as water borne. This involves a consideration of the Mills-Reincke phenomenon and the Hazen theorem (Sedgwick-MacNutt), and the ideas of chronic intestinal tract infection advanced by Hill and Whitcomb. It means a careful analysis of all available

and reliable vital statistics of those communities having impure water supplies as well as those having pure supplies.

(2) A clear definition of what really constitutes a pure drinking water. This means that much light is needed upon the relative numbers and kinds of bacteria, the nature and amount of the organic and inorganic matter which may be present in public water supplies, and their significance in the causation of disease. It necessitates an examination of the available bacteriological and chemical data of public water supplies, and a classification of the same in relation to vital statistics.

(3) The selection of the maximum limits for the numbers and kinds of bacteria in a drinking water, and the permissible amounts of organic and inorganic matter which such a water may contain.

STANDARDS FOR SEWAGE AND SEWAGE EFFLUENTS

The Eighth Report of the Royal Commission on Sewage Disposal (*Nature*, 91, 61) deals with the important question of standards and tests for sewage and sewage effluents discharging into rivers and streams. The Commissioners had earlier indicated the desirability of fixing a legal standard for sewage effluents, and proposed that such a standard should be based upon (1) suspended solids and (2) absorption of dissolved oxygen. Their contention then was that the two tests should be taken separately, and they suggested three parts per 100,000 as the limit of suspended solids, and that the effluent after removal of its suspended solids should not absorb more than 0.5, 1 and 1.5 parts dissolved oxygen per 100,000 after one day's, two days', and five days' incubation at 65° F., respectively. In their present Report the Commissioners recognize the difficulty of the separation of the suspended solids, and finally recommend the following as the normal legal standard, namely: 3 parts per 100,000 of suspended solids, and, including its suspended solids, the effluent shall not absorb more than 2 parts dissolved oxygen per 100,000 after five days' incubation at 65° F. In the opinion of the Commissioners, the legal standard should be a variable one, dependent upon the conditions at the outfall, i. e., the condition of the river or stream receiving the effluent and the relation of the volume of sewage effluent to river water.

The Commissioners state that their experience leads them to think that if the dilution while not falling below 150 volumes does not exceed 300 volumes, the dissolved oxygen test may be omitted and the standard for suspended solids fixed at 6 parts per 100,000; and if the dilution while not falling below 300 volumes does not exceed 500, the standard for suspended solids may be further relaxed to 15 parts per 100,000. With a dilution of more than 500 volumes all tests might be dispensed with and crude sewage discharged, subject to such conditions as to provision of screens or detritus tanks as might appear necessary to the central authority.

"HARDENED" OILS

A. W. Knapp (*Analyst*, 38, No. 444, 102) described three fats which were obtained from a clear cottonseed oil. They were hardened by hydrogen with the aid of different catalysts, and gave the following results upon examination:

CATALYST	Percentage of catalyst in oil	Character of product	Butyro-refraction (corrected to 40° C.)	Melting point. ° C.
Nickel.....	1.00	Hard	45.7	49
Platinum.....	0.10	Hard	47.8	46
Palladium.....	0.06	Brittle	45.5	52

The keeping properties of these "hardened" oils were said to be remarkably good. The fats described had been prepared for nearly a year and a half, had often been exposed to damp air, and yet showed no signs of rancidity. The free acidity (0.70 per cent. as oleic acid) had not appreciably changed.

Knapp states that hardened oils give soaps which are good in color, but deficient in lathering properties. He does not consider that any objection will be raised to their admixture with other fats for soap-making. However, he points out that their use in the preparation of edible fats is more open to question, and that in the interests of public health, certain investigations should first be made to show:

(1) That no harmful substances are produced by the chemical changes in the fatty glycerides and unsaponifiable matter.

(2) That a high percentage of tristearin does not render the fat indigestible.

(3) That traces of nickel, from 1 to 10 parts per million, are not harmful.

He considers that there is perhaps little to be feared from objectionable substances in the hydrogen used, as the majority of such substances would poison the catalyst.

WATER GAS TAR AS A WOOD PRESERVATIVE

At the Fifth Annual Meeting of the Indiana Gas Association, Indianapolis, Ind., March 12, 1913, F. C. Mathers presented the results of some experiments on the preservation of timber with water gas tar. The United States Forest Service has conducted many experiments on the creosoting of wood, but none of the Bulletins issued gives results with water gas tar, although, Mathers stated, fence posts, etc., could be treated with this tar which costs only about 3 cents per gallon as compared to 15 cents per gallon for coal tar creosote. Mathers found that water gas tar would render timber water-proof, although it was less strongly antiseptic than coal tar creosote; and timber exposed to the weather became very much more resistant to decay after receiving treatment with water gas tar.

KIND OF WOOD TREATED	Per cent. of tar absorbed	Gallons of tar for one post	Cost of tar per post in cents
Sycamore(a).....	65	4.0	12
Black walnut(b).....	168	3.6	11
Sugar maple.....	39	1.9	6
Beech.....	45	4.2	13
Wild cherry.....	48	2.4	7
White cedar.....	34

(a) The best wood to treat, owing to the ready absorption.

(b) Partly decayed, hence large absorption.

The table above gives the percentage by weight of tar absorbed, the number of gallons required for a post 7 feet 6 inches long and 4 inches in diameter at the two ends, and the value of the tar in each post, assuming the cost of the tar to be 3 cents per gallon. One gallon of water gas tar was found to weigh 8.9 pounds.

(At the Fourteenth Annual Convention of the American Railway Engineering Association, Chicago, March 18, 1913, a committee reported that the use of water gas creosote was limited but increasing, and that there was a growing sentiment in favor of mixing this with coal tar creosote. The principal objection to the use of water gas creosote seems to have been its unauthorized use in the adulteration of coal tar creosote.—W. A. H.)

PULP AND OTHER PRODUCTS FROM WASTE RESINOUS WOODS

It has been demonstrated, both in the laboratory and in the mill, that paper of good quality can be made from pine wood (Bureau of Chemistry, *Circular* 41 and *Bulletin* 144). Veitch and Merrill (Bureau of Chemistry, *Bulletin* 159, 1913) now consider that it is feasible to combine three well developed chemical industries—paper making, wood distillation (in a modified form), and the manufacture of rosin oils—and thus to obtain from a single raw material, waste resinous wood, practically all the valuable constituents. The country's sources of paper, turpentine, rosin oils, and wood alcohol can be greatly augmented and the injury to forests by fire and insects materially reduced by the utilization of this wood.

The approximate yield for 4,000 pounds of cord air-dry wood

(3,200 pounds moisture-free wood) of the valuable products and the value of each is thus given by Veitch and Merrill:

Refined wood turpentine, 6 gallons, at \$0.40.....	2.40
Pine oils, 7 gallons, at \$0.35.....	2.45
Rosin spirits, 11 gallons, at \$0.20.....	2.20
Rosin oils, 10 gallons, at \$0.35.....	3.50
Phenoloids, 12 gallons, at \$0.06.....	0.72
Crude methyl alcohol, 3.5 gallons, at \$0.35.....	1.20
Unbleached pulp, 1,440 pounds, at \$0.0175.....	25.20
Total.....	48.17

Thus products worth \$48.17 are made from wood which costs from \$2.00 to \$4.00 delivered at the works. The values given are approximate wholesale values at the plant, and are said to hold, approximately, for good average lightwood, except as to refined wood turpentine, which should run higher than reported. All the products are said to be of good quality, the pulp making a good strong brown wrapping paper, quite similar to that now selling at from 3 to 4 cents per pound.

It is believed that such a combination as that mentioned offers the most profitable use of refuse wood and stumps on the cut-over pine lands of the South and West.

THE EFFECTS OF TAR ROADS UPON VEGETATION AND ANIMALS

It has been stated that the dust from tarred roads has appeared to be more irritating to the eyes than that from untarred roads, and in 1910 an investigation of this matter was conducted in France by Truc and Fleig (*Compt. rend.*, 151, 593). It was ascertained that dust from untarred roads had only the slightest effect when sprinkled on the eyes of animals, and that dust from old tarred roads, from which the coating had more or less disappeared, gave effects little different. However, dust from old tarred roads with a well preserved surface occasioned conjunctivitis and other lesions, while dust artificially produced from such roads gave still more severe effects. Notwithstanding the fact that bituminous vapors have only a slight action upon the eye (*Compt. rend.*, 151, 769), the investigations of Truc and Fleig seemed to show that the results corresponded to the proportion of tar, as well as to the mechanical irritation produced by the dust and to the germs present. Concerning these observations, Baskerville has remarked (*N. Y. Med. J.*, November 30, 1912) that while bituminous dust may rapidly produce various lesions in the eyes, and may leave persistent leucoma, the condition of the eye and the action of sunlight are both predisposing causes. He noted that the experiments which have been conducted on these points do not, moreover, constitute an argument against the tarring of roads, for, when tarring is well done, it diminishes the chance of injury to the eyes.

In 1911, Mirande (*Compt. rend.*, 152, 204) investigated the many substances prepared from coal tar used for preserving wood, destroying moss on tree trunks, as insecticides, etc. He was led to conclude that these all contained creosote and gave off vapors which were destructive to leaves, flowers, shoots, etc., in the same way as coal tar vapors, blackening them and causing death by plasmolysis. Quite recently the statement that the use of tar on roads has an injurious effect on the surrounding trees and vegetation, for which Mirande is held responsible, has been pronounced to be unfounded by German experts: H. F. Fischer has been investigating the matter, and he plans to present his results before the coming International Road Congress, which is to convene in London in June, 1913. It may also be noted that the conclusions of Mirande respecting tarred roads have been refuted by several French engineers (*Chem. World*, 2, 106), who point out that a large street in Bordeaux has been treated with tar for some years without the slightest damage to the trees bordering the street, and that other towns have also practised tarring without injurious results, though one example is on record where the trees around a square were destroyed by tar.

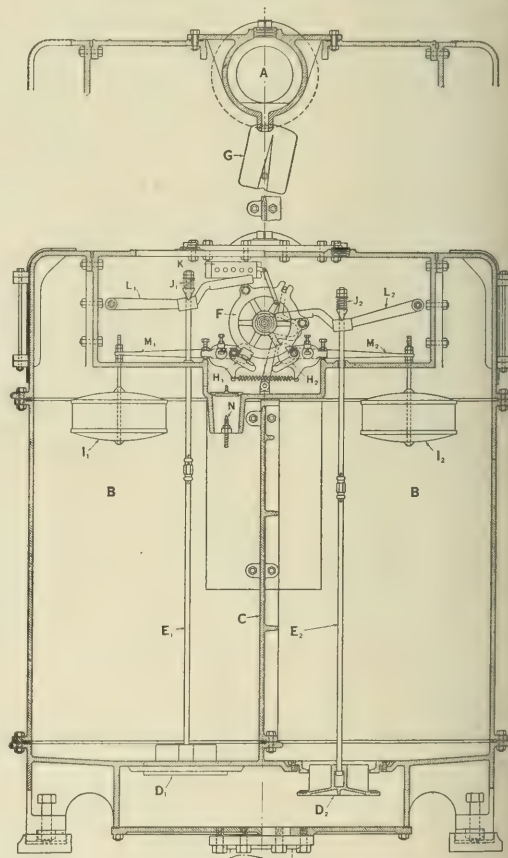
In this case—at Fontenoy de Comte—the tar was spread so close to the trees that it prevented the water from getting to the roots.

PRESSURE FILTERS FOR CLARIFYING TRADE WASTES

The clarification of the liquid wastes from a glue factory by means of pressure filters has been tried out by a Gloucester, Mass., firm, and a plant with a capacity of one million gallons per day has been installed at its works. The wastes are pumped from a basin by a centrifugal pump and passed through pressure filters until the layer of waste which is intercepted by the top surface of the sand has attained a considerable thickness. The water is then drawn off and compressed air is applied to dry the sludge layer and convert it into a flexible cake, which is rolled up and removed through manholes in the filter. After passing through presses, the sludge cake may, it is claimed, be used as a fertilizer. The pressure filters are cylindrical steel drums containing a bottom layer of pebbles and a filling, 30 inches deep, of coarse quartz sand. In drying the sludge layer, in which operation air under pressure is blown down through the filtering medium, forcing the water out, about one hour is required. The filters are operated continuously for 60 working hours at a time, and are then opened up and the detritus is removed. It is needless to remark that the time of the drying process is dependent upon the blower.

THE HAMMOND WATER METER

The Hammond meter, designed for use under the exacting



conditions found in the modern power station, is said to be

unaffected by water containing oil or mud and to be capable of measuring liquids of any temperature. It is claimed that it can be used in any case where the liquid to be measured can flow from the meter by gravity, and that it is especially useful in measuring condensation from engines, the supply of water to boilers, liquids from vacuum pans, chemicals, brine, volatile oils, creosoting liquors, sugar juices, etc.

The Hammond water meter is constructed entirely of cast iron sections bolted together, and its operation is as follows:

The meter consists of two tanks, comprising an upper receiving tank, A, located in the top part of the meter, and a lower measuring tank, B, divided into two compartments, "right" and "left," by means of a central vertical partition, C.

The liquid enters the receiving tank and flows through a slot in the bottom, into the measuring tank B. This measuring tank has discharge valves D_1 and D_2 opening downward from each compartment, which are held up to their seats by valve rods E_1 and E_2 , operated by lever arms L_1 and L_2 .

The tilting inlet valve G is operated by the wrist plate, causing the water to be deflected either into the "right" or "left" compartment. With the tilting valve G and the wrist plate F in the position shown, and the water flowing into the left measuring tank, the operation is as follows:

The discharge valve D_1 is held up to its seat by the wrist plate F which is held by the latch H_1 .

As the water rises in this compartment it lifts the float I_1 , which, through lever M_1 , unhooks the latch H_1 , and releases the wrist plate. The weight of the water on the discharge valve D_1 instantly pulls down the valve and rotates the wrist plate. This turns the tilting inlet valve G to deflect the water into the "right" measuring tank B. At the same time it draws up the discharge valve D_2 to its seat, where it is held by the latch H_2 , ready for the water now flowing into the "right" compartment.

The springs J_1 and J_2 in the heads of the valve rods E_1 and E_2 hold the discharge valves up to their seat and keep them from leaking.

The wrist plate and latches are provided with hook blocks similar to those on the valve gear of a Corliss engine, and are made of hardened steel. The wrist plate is mounted on ball-bearings as are also the rollers on the rim of the wrist plate on which the levers controlling the valves roll.

The operation of the meter is automatic and continuous. A record of the cycles of operation is registered on the revolution counter K.

SCIENTIFIC SOCIETIES

THE OFFICIAL CLOSING OF THE EIGHTH INTERNATIONAL CONGRESS

The Executive Committee of the Eighth International Congress of Applied Chemistry met at the call of President Nichols at the Waldorf-Astoria on Friday, April 18th, at which time the reports of the secretary and the treasurer were presented and accepted. Other official business was transacted, and the final resolution adjourning the committee *sine die* was passed, thus officially closing the Congress. After the business meeting, Dr. and Mrs. Nichols entertained the members of the Committee and their wives at dinner.

The following evening the representative chemists of America tendered a complimentary dinner to Dr. Nichols and Dr. Hesse at the Chemists' Club. The banquet was held in Rumford Hall which was crowded to its capacity. Many chemists both here and abroad were unable to attend, but expressed in innumerable letters and telegrams their appreciation of the labors of the distinguished officers of the Congress.

Professor E. W. Morley, Honorary President of the Eighth Congress, presided and introduced the Toastmaster, Dr. Arthur D. Little, President of the American Chemical Society. After a glowing tribute to the work of the guests of honor, Dr. Little introduced Professor Wilder D. Bancroft, of Cornell University, who responded to the toast of "The Chemists of America." Dr. William Brady, Chief Chemist of the Illinois Steel Company, spoke to the toast of the Manufacturers of America, and Dr. Leo H. Baeckeland to the toast, "Was it Worth While?"

Dr. David T. Day, of the Geological Survey, was called upon and in a most eloquent tribute presented to Dr. Nichols, on behalf of the Chemists of America, as a mark of their appreciation of his unswerving fidelity to the welfare of Chemistry in the United States and his self-sacrificing service in behalf of the Eighth Congress, a duplicate of the British Treasury Ink-Stand and Desk Set, executed in silver by Tiffany, and to Dr. Hesse, for his distinguished success in the execution of the many and responsible duties as Secretary of the Congress, and as an appropriate mark of the high esteem of his colleagues in the profession he represented so creditably, a magnificent Loving Cup.

Both Dr. Nichols and Dr. Hesse spoke feelingly in expressing deep appreciation to the chemists for their coöperation and as-

sistance in the work of the Congress, and the happy choice of the method selected by them for expressing their approval of the work done in this great undertaking.

THE UNITED STATES PHARMACOPOEIA—THE PROGRESS OF THE NINTH REVISION¹

By JOSEPH P. REMINGTON

Received March 25, 1913

The conditions now existing in the United States have been a compelling cause for a change of method in conducting the present Revision of the Pharmacopoeia. The directions of the Convention that an Executive Committee of fifteen shall be organized to have immediate charge of the work of Revision have now been in operation for nearly three years. With the enormous amount of detail, it became necessary to divide the work and give to each of the fifteen of the Executive Committee the position of Chairman of the Sub-committees having charge of the fifteen different divisions. Each Chairman reports monthly to the General Chairman the condition of the work in his Sub-committee; in this way correlation is secured. The General Committee of Revision is, of course, to be depended upon to comment, criticize or correct the report of the Executive Committee. The By-laws provide that an appeal to the General Committee of Revision through the Executive Committee or the Chairman can be made in case of difference of opinion.

Probably the greatest change in the method was the means now employed to reach a correct decision, particularly with regard to the tests for chemical substances and to provide standards. In previous Revisions, the Committee had to obtain information from manufacturing chemists and others not on the Committee by special correspondence and requests for information, but the most important questions remained unanswered because the manufacturer preferred to keep this information to himself. In very few cases it was necessary to confirm or disprove the information given by writing to a competitor. The present method is far more effective on account of the Pure Food and Drug Acts, and hearings on important subjects have been held by parties interested in the manu-

¹ Address before the Division of Pharmaceutical Chemistry, American Chemical Society, 47th Meeting, Milwaukee, March, 1913.

facture of a product. Instead of trying to drag information out of the manufacturer, the method now used is to call for a hearing at a conference of all parties interested. After a sufficient time is given to discuss and ventilate the subject from all points of view, the manufacturers are asked to draw up in writing their conclusions and these are reported to the Chairman of the Sub-committee. This does not prevent any manufacturer from objecting to the report of the conference, for he has the right to present his views in order that the Chairman of the Sub-committee may hear and consider the dissenting opinion. The tests are then to be passed upon by the Executive Committee and submitted to the General Committee of Revision. While it is understood that the Pharmacopoeia Committee is not bound by the action of the conference of manufacturers, the practical result is that before the book is issued the fullest information is before the Committee. In addition to this, all changes from the Eighth Revision of the book in tests or standards will be published in the pharmaceutical and chemical journals and communications sent to the Chairman will be referred to the proper Sub-committee for due consideration. It is believed that by this simple method errors will be avoided and the manufacturer will have ample time to arrange his stock before the date fixed for the new Pharmacopoeia to go into effect. There will undoubtedly be differences of opinion on some of the details and manufacturers will find fault with some of the standards or tests. But as compared with the previous methods of revision, it must be admitted by all that the new method will have a tendency to lessen the number of complaints which have been made heretofore under the old plan. No originality, of course, can be claimed for this plan, for it is based upon similar methods adopted by Legislatures, the United States Congress and other bodies. Of the hearings which have been had, when a manufacturer proposes to make some changes which will favor his own product only, counter-propositions are made by the others and a frank discussion is held. In most cases a test has been proposed which can be reasonably followed by all reputable firms. Before the book is issued, the Government tests and standards will be subjected to conference conclusions and the results of the analyses of Government and State chemists will be brought into harmony, if possible, for there should be no conflict of standards. The dishonest, careless manufacturer cannot expect consideration for it is believed that the courts will rule with greater stringency than ever, but the standards must be upheld.

The Food and Drug Laws have vastly improved the quality and purity of chemical substances and this work of improvement must be continuous and no retrogression should be promoted. The purity rubric system inaugurated in the present Pharmacopoeia will be continued and of course some changes will be made raising the quality of the official products. From correspondence from several sources, it appears that the rubrics are not thoroughly understood. In every case, the rubric fixes the minimum requirements and the words "not less than" are used. A manufacturer can improve his product to any extent that he desires. If the Pharmacopoeia requires that a chemical shall contain not less than 99 per cent of product, he can sell a 100 per cent product and get all the commercial advantage that he wishes, but he is restrained from selling a 98 per cent product. The tests which are obtained are based upon the percentage contained in the rubric.

Up to the present time 673 articles out of 853 have been reported upon to the Executive Committee and are ready for submission to the General Committee. The remainder of the articles are nearly ready for a tentative hearing. These, of course, are all subject to comment and criticism and it is because of this fact that the Chairman cannot fix a date for the issue of the book. It all depends upon how much of the work of the Committee must be revised and what the changes are to be.

Obviously, no one can even guess at the amount of time which will be required to adjust all conditions, but it is not likely that many changes will be asked for.

The following table shows the number of pages of official Bulletins, Letters, and Circulars issued by the various Sub-committees and Committees, although the communications from firms, corporations, physicians, pharmacists, scientific bodies, and the public generally, and the replies thereto are not included in the summary, although they constitute a large amount of correspondence.

SUB-COMMITTEE BULLETINS		Pages
No. 1—Scope		288
No. 2—Therapeutics, etc.		166
No. 3—Biological Products, etc.		80
No. 4—Botany and Pharmacognosy		252
No. 5—Inorganic Chemistry		430
No. 6—Organic Chemistry		797
No. 7—Proximate Assays		270
No. 8—Volatile Oils		89
No. 9—Fluid and Solid Extracts		315
No. 10—Waters and Spirits		313
No. 11—Syrups and Elixirs		260
No. 12—Ceresates and Ointments		62
No. 13—Miscellaneous Galenicals		177
No. 14—Tables, Weights, and Measures		75
No. 15—Nomenclature		58
Executive Committee Letters		1763
General Committee Circulars		847
Total		6272

As stated above, the proposed text for 673 articles has been before the Executive Committee. These articles, after consideration by the Executive Committee, are being presented in redrafted form to the General Committee of Revision for comment. All remaining articles for the text are in the hands of the Sub-committees and their revision is being rapidly pushed to completion. The General Article on Proximate Assays and a number of the assay processes for vegetable drugs have been submitted. A report on Average Doses has been made. Practically all of the Tables for the Appendix are before the Committee. A full report on Diagnostical Reagents and Clinical Tests has also been made.

1832 PINE STREET,
PHILADELPHIA, PA.

DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS, AMERICAN CHEMICAL SOCIETY

MILWAUKEE MEETING, MARCH 24-27, 1913

The Industrial Division met at Marquette University, Milwaukee, Wis., March 26 and 27, 1913, with vice-chairman George P. Adamson presiding and S. H. Salisbury as acting secretary.

The minutes of the Washington meeting were read and approved as also were the minutes of the meeting of the Executive Committee.

The report of the Committee on Standard Specifications and Methods of Analysis was read by the secretary and accepted.

The following committees made no report: Analysis of Soap Products and Glycerine; Research Problems; Definition of Trade Terms; Special Compounds; Professional Code of Ethics; Publicity.

There being no further business to come before the division, the reading of the papers was proceeded with as follows:

1. **Analysis of Glucose and Starch Sugars.** EDWARD GUDEMAN.
2. **The Training of the Fermentologist.** CARL A. NOWAK.
3. **The Training of the Technical Chemist.** JOHN S. STAUDT. This

paper provoked a very lively discussion in which the following members took part: Messrs. Parsons, Comey, Parr, Staudt, McCoy, McCormack, Gray, Frary, Brady and others. The points discussed were the salaries which graduating chemists are able to obtain in starting work and the feasibility of

students getting practical work during summer vacations.

4. **The Determination of Zinc in Treated Ties.** FRANCIS C. FRARY and M. GORDON MASTIN.

Discussed by Mr. Salmon, Mr. Wallace and others.

5. **Preliminary Report upon a Practical Accelerated Test for Paints and Varnishes.** A. M. MUCKENFUSS.

6. **Concrete Analysis.** OTTO M. SMITH.

7. **Fuller's Earth—Its Occurrence, Mining, Preparation, Use and Recovery.** CHARLES L. PARSONS.

8. **The Uranium, Vanadium and Radium Situation.** CHARLES L. PARSONS. This paper was followed by a talk by Dr. Moore, of the Bureau of Mines, who discussed the occurrence of the uranium ores and the outlook for the production of radium in this country.

9. **Coal Ash.** S. W. PARR.

10. **The Specific Heat of Coal and its Relation to the Presence of Combined Water in the Coal Substance.** HORACE C. PORTER and GUY B. TAYLOR.

11. **A Simple Gasoline Gas Generator for Sulfur Determinations.** C. E. WATERS. Read by Mr. Tuttle.

12. **Determination of Sulfur in Illuminating Gas.** R. S. MCBRIDE and E. R. WEAVER. Read by Dr. Hildebrand.

13. **The Determination of Sulfur in Ammonium Sulfate with Special Reference to the Determination of Sulfur in Illuminating Gas.** R. S. MCBRIDE and E. R. WEAVER. Read by Dr. Hildebrand.

The Thursday morning session was devoted to a general experience meeting. Dr. Hildebrand gave an informal talk on platinum and the work of the Platinum Committee which was afterward discussed by P. H. Walker, S. W. Parr, A. D. Little and C. L. Parsons, particular stress being laid on the restriction of the use of platinum in the jewelry trades.

Mr. Hess asked for information as to why arsenious oxide in storage should be injurious to the health of workmen. Dr. Sy replied that it might be due to the formation of arsine as a result of bacterial action.

Mr. A. D. Little and Mr. G. P. Adamson discussed the increased use of saltcake in the manufacture of paper pulp and its probable effect on the available supply and price.

Mr. Bennet desired information as to the construction of furnaces for the reduction of barium sulfate for the manufacture of lithophone.

Dr. Staudt and Mr. Gray discussed gasoline as to the future available supply and tendency of the price.

A. D. Little described several devices used in his laboratory in connection with analytical work.

Dr. Bancroft talked on cellulose analysis and Dr. J. C. Hartzell discussed the abuse of the bodily organs by solids dissolved in water.

The chairman spoke of the financial condition of the section and requested the secretary to write to each member of the division asking for a voluntary contribution of one dollar and also to make requests for more papers for the meetings of the division.

MEETING OF THE EXECUTIVE COMMITTEE

The Executive Committee of the Division of Industrial Chemists and Chemical Engineers met, March 26, 1913, and elected S. H. Salisbury, Jr., to fill the vacancy caused by the resignation of F. E. Gallagher.

S. H. SALISBURY, JR., *Secretary*

DIVISION OF FERTILIZER CHEMISTRY. AMERICAN CHEMICAL SOCIETY

MILWAUKEE MEETING, MARCH 24-27, 1913

Meeting called to order by the chairman, Mr. Rudnick. On motion it was decided to proceed to the program:

A Simple Method of Preparing Neutral Ammonium Citrate Solution. ANDREW J. PATTEN.

On motion, the work on ammonium citrate was referred to the Phosphoric Acid Committee, with a request that they bring the subject before the A. O. A. C.

On motion the Phosphoric Acid Committee were requested to confer with Dr. J. H. Hildebrand in regard to working out

a practical method for determining Neutral Ammonium citrate and Phosphoric Acid compound by hydrogen electrode.

REPORT OF COMMITTEES

The Committee on Nitrogen. PAUL RUDNICK, *Chairman*

This committee has prepared a sample of commercial nitrate of soda for cooperative work. Some work has been done by the committee on the analysis of this product, chiefly by the official modified Gunning and Kjeldahl methods. This work is not quite completed, but it is expected that the sample will be ready for distribution for cooperative work outside of the committee very shortly and that a report on this work will be ready for the next meeting. Report accepted.

The Committee on Potash. J. E. BRECKENRIDGE, *Chairman*

The committee report was accepted and is published in full in this issue. The matter of the attitude of the government on the distilling of denatured alcohol for laboratory work was referred to the Committee on Potash, with instructions to obtain a formal government ruling on the proposition as applied to this work.

The Committee on Phosphate Rock. F. B. CARPENTER, *Chairman*

The Committee on Phosphate Rock had done no cooperative work since the last meeting of the division, and had, therefore, nothing to report relative to past investigations.

Mr. Hagedorn, Chairman of the Sub-committee on Phosphoric Acid, is preparing a sample of phosphate rock to be sent out for further study of methods of analysis, including determination of phosphoric acid, iron and alumina and moisture.

The committee has received a number of requests from chemists interested in phosphate rock, for a standard sample of this material. In response to these requests, the committee has decided to adopt as a tentative standard, a sample of phosphate rock on which a large number of results have been obtained in cooperative work by members of this division under the direction of the committee. The average results obtained in this cooperative work will be furnished with this sample and while these results may not be absolutely correct, yet they are undoubtedly very close to the truth, as they represent an average of the best results obtained, most of them from analysts specializing in this line of work, with the elimination of obviously erratic results. This standard should serve to bring about a greater uniformity in results, both by enabling those interested to check the work on analysis, as well as by enabling the individual analyst to check his own work with a sample of known composition. Samples may be obtained from Mr. C. F. Hagedorn, Armour Fertilizer Works, Union Stock Yards, Chicago, Ill., by enclosing 25 cents to cover cost of packing, mailing, etc.

Report was accepted. On motion the meeting adjourned.

J. E. BRECKENRIDGE, *Secretary*

REPORT OF COMMITTEE ON POTASH. FERTILIZER DIVISION. AMERICAN CHEMICAL SOCIETY

MILWAUKEE MEETING, MARCH 24-27, 1913

The Work has been mapped out as follows:

I. To compare results with denatured alcohol as found in the trade with results with pure alcohol as usually used for potash determinations.

II. Official Method for mixed fertilizers as applied to potash salts.

Samples to be analyzed were:

1. High-grade sulfate potash.
2. Muriate potash.
3. Kainit.
4. Complete fertilizers about 10 per cent. K_2O .

Work to be done was:

1st Test 1, 2, 3, 4, by regular official method.

2nd Test the same by regular official method, using denatured alcohol instead of pure alcohol.

3rd Test same by modified method (U. S. Dept. of Agr., Bureau of Chem., *Bull.* 152, page 41) using pure alcohol.

4th Test same by Modified method using denatured alcohol.

5th Test potash salts by modified method for mixed fertilizers. As this work was outlined for 1911, the regular official method refers to official method for 1911 which in 1911 was changed, and the modification adopted as official (*Circular 108*, Bureau of Chem., U. S. Dept. of Agr.).

The work done was by the committee, and no samples were distributed.

The results were as follows:

	Muriate K ₂ O Per cent.	Sulfate K ₂ O Per cent.	Kainit K ₂ O Per cent.	Mixed fertilizer K ₂ O Per cent.
Official method:				
Pure alcohol.....	48.84	53.08	13.54	9.19
Official method:				
Denat. alcohol.....	48.88	53.04	13.68	9.27
Modified method:				
Pure alcohol.....	49.08	53.00	13.58	9.26
Modified method:				
Denatured alcohol.....	49.26	53.08	13.58	9.32
Method for mixed fertilizers: (a)				
Denatured alcohol.....	47.56	50.64	13.58
Method for mixed fertilizers: (b)				
Denatured alcohol.....	49.20	53.08	13.64	{ 9.30 9.31

(a) Dishes uncovered during ignition.

(b) Dishes covered with fused silica plate during ignition.

REMARKS.—The results, especially in the case of the sulfate, show no variations due to use of pure or denatured alcohol. The muriate and mixed fertilizer show slight differences, which may be accounted for in other ways.

I have used denatured alcohol for over a year and have found it very satisfactory in every way.

In testing the potash salts by the method for mixed fertilizers, two sets of determinations were made: (A) during ignition the platinum dishes were uncovered; (B) dishes were covered with fused silica plates.

From the low results obtained by method (A) it is evident that there is a decided loss of potash during ignition when the dishes are uncovered.

The results by method (B), where the dishes were covered, check closely all the other determinations.

From this work it appears that the theory, that the method for mixed fertilizers gives more accurate results than the official method, when applied to potash salts, does not hold good. When the ignitions are carefully made without loss, the results check those which are obtained without the use of ammonia and ammonium oxalate, where no ignition is necessary. It seems that there is nothing further to be gained by testing this method.

E. L. BAKER, *New York Expt. Station, Geneva*

Samples not the same as Mr. Baker's:

	Muriate K ₂ O Per cent.	Sulfate K ₂ O Per cent.	Kainit K ₂ O Per cent.	Mixed fertilizer K ₂ O Per cent.
Modified method:				
Pure alcohol.....	50.15	53.65	13.45	9.20
Modified method:				
Denatured alcohol.....	50.25	53.50	13.50	9.23
Modified method:				
Mixed fertilizer as applied to potash salts.....	48.72	52.44	13.50

Variations, in case of muriate 0.10 per cent, sulfate 0.15 per cent, kainit 0.05 per cent, mixed fertilizer 0.03 per cent between pure alcohol and denatured alcohol.

Large loss on sulfate and muriate when method for mixed fertilizers is applied to potash salts.

J. E. BRECKENRIDGE, *American Agricultural Chemical Co.*

CONCLUSIONS

From the work done, we believe the use of denatured alcohol worthy of consideration, and that accurate potash determinations can be made by using same instead of pure alcohol with a large saving in expense to the industrial laboratories.

Method for mixed fertilizers applied to potash salts gives low results unless dishes are covered during ignition.

RECOMMENDATIONS

Further work on denatured alcohol.

Work with perchlorate method for potash.

Investigation of double manure salts as to the content of magnesium and insoluble material.

Massachusetts reports in *Bulletin 143*, MgO 8.98 per cent, insoluble matter 21.60 per cent.

Same samples analyzed in Amer. Agric. Chem. Co.'s laboratory gave:

No.		Per cent.		Per cent.
1	Insoluble	15.83	MgO	5.98
2	Insoluble	18.22	MgO	5.31
3	Insoluble	0.54	MgO	12.56
4	Insoluble	9.85	MgO	6.59

K₂O content was equal to guarantee in all cases.

J. E. BRECKENRIDGE, *Chairman*

RESEARCH FUND, AMERICAN ELECTROCHEMICAL SOCIETY

In order to further the objects of our society as given by our constitution, it has seemed wise to try the experiment of assisting purely scientific research work in electrochemistry where this is done under conditions which would make the application of a few hundred dollars annually an effective and efficient assistance.

For this purpose, \$150 is made available for the next year, to be given in whole or in part to help members of the society who need such assistance to carry on some predetermined work.

The committee does not wish to burden the scheme with unnecessary rules or requirements, and propose to carefully consider requests for this assistance on the merits of the case as it may be presented. If the further developments of the scheme warrant the issuing of limitations on the distribution of the fund, such will be published.

The committee's aim will be to give assistance to those who are apparently equipped to do effective work along those purely scientific lines which are not usually explored by commercial or industrial organizations. In other words, we wish to advance the science of electrochemistry.

The research work thus assisted must be published in the transactions of the society.

Applications may be sent to the chairman of the committee and should be received before August first.

W. R. WHITNEY, *Chairman*

W. H. WALKER

F. A. J. FITZGERALD

OBITUARIES

DR. FRIEDRICH W. C. SCHNIEWIND

On March 12th, Dr. Friedrich W. C. Schniewind passed from this life at his home in Englewood, N. J. An operation for appendicitis, which he had successfully withstood and from which

he was thought to be recovering, was followed by unforeseen and fatal complications.

Dr. Schniewind was born at Bochum, in Westphalia, October 23, 1861. By training he was a chemist, having studied at the

institutes of technology at Charlottenburg and Munich and at the Universities of Berlin, Munich and Heidelberg. From the latter he received the degree of Ph.D. After some experience as a blast furnace chemist in Westphalia, he came to this country in 1889, and conducted analytical laboratories at Cleveland, Ohio, and at Crystal Falls, Mich.

He then became interested in the by-product coke oven process, and acted as the American representative of Dr. C. Otto & Co., of Dahlhausen, Germany. About 1894, the Otto Coke & Chemical Co. was organized to introduce ovens of the Otto type into this country, and a plant, one of the earliest to be erected here, was built at Glassport, Pa. Dr. Schniewind acted as chemist and superintendent, and his association with the gas industry may be said to date back to this period.

His clear vision and scientific mode of thought soon recognized

the tremendous future before the by-product coke oven industry, not only in its primary field as a source of blast furnace coke, tar and ammonia, but also in the use of coke for other fuel purposes and of the surplus gas for illuminating. The main difficulty with the latter suggestion, namely, the low candle power of the gas, he proposed to overcome by the method of division of gases, then new and untried, since became a well-recognized method of operation. Dr. Schniewind investigated the possibilities of this procedure with characteristic thoroughness, both theoretically and experimentally, and was able to enlist the active financial support of such men as Henry M. Whitney and the late William L. Elkins, Jr.

The United Coke & Gas Co. was organized to succeed the original company, and in 1898-9 the 400-oven plant at Everett, Mass., the largest of its time, was built, embodying the principle of the division of gases. The result of Dr. Schniewind's research, which he presented in a paper on "The Production of Illuminating Gas from Coke Ovens" before the Inter-

national Engineering Congress at Glasgow, in 1901, may be said to have first placed the matter fairly before the scientific world. It aroused much comment, not all favorable, but at the present time nearly, if not all, of the coke oven plants in the United States operate on this principle, where it is commercially feasible to dispose of illuminating gas. It has also been adopted in a number of plants in England and Germany. Within a year or two such a plant was equipped to supply illuminating gas to Bochum, Germany, Dr. Schniewind's birthplace. His championship of this principle, however, was only a tithe of his activities in his chosen field. He acted as consulting chemist, later manager and vice-president, of the United Coke & Gas Co., engaged actively in the construction of by-product coke oven plants, and into

this work he put his whole heart and soul. His acquaintance among the leading men in the steel and gas industries became very wide, and his abilities were universally recognized.

At the time of his death, Dr. Schniewind was president and sole owner of the German-American Coke & Gas Co., and its subsidiary companies, the United Coke & Gas Co. and the American Coke & Gas Construction Co., as well as president of the newly organized Schniewind Coke Oven Co.

Dr. Schniewind was a voracious reader and a constant student. Although born a German, he used the English language with unusual accuracy and clearness. He collected and maintained an extensive scientific library, which included almost everything obtainable on coal carbonization and by-product utilization. Those who have worked with him can testify to his wide reading and his wonderful memory for facts. He was the author

of a number of scientific papers on coal carbonization, coke production, ammonia, benzol enrichment, etc., as follows: "The Otto-Hoffmann Retort Coke Oven System," Sept. 6, 1894, *Iron Age*.

"Gas from By-product Coke Ovens," *Iron Age*, 1895, page 463.

"The Everett Coke Oven Gas Plant," *Prog. Age*, Aug. 15 and Sept. 1, 1899, and Jan. 1, 1900.

"Otto-Hoffmann Coke-Oven Practice," *Amer. Gas Light Jour.*, Mar. 25, 1901.

"Production of Illuminating Gas from Coke Ovens," Paper before the International Engineering Congress at Glasgow, 1901.

"The Manufacture of Coke in U. S., with special Reference to the Markets for By-products," *Mineral Industry*, 1902, Vol. X, p. 135.

"By-product Coke Ovens," *Mineral Industry*, 1903, Vol. XI, p. 158.

"Benzol Enrichment with Reference to Coke Oven Gas," *Prog. Age*, May 15, June 1 and 15, 1905.

Many patents were allowed to Dr. Schniewind bearing upon this industry, of which we mention the following:

- 627,595, Coke Ovens and Method of Operating Same.
- 644,368, Apparatus for Transferring Heat from one Fluid to Another.
- 644,369, Regenerative Coke Oven.
- 668,225, Apparatus for Manufacturing Gas.
- 673,928, Regenerative Coke Oven.
- 684,590, Method of Enriching Gas.
- 698,062, Method of Manufacturing Gas.
- 698,063, Plant for Manufacturing Gas.
- 723,493, Double Coke Producer.
- 728,991, Process of Enriching Gas.
- 820,525, Method of Treating and Utilizing Gases.
- 845,719, Apparatus for Charging Coke Ovens.
- 976,929, Burner for Coke Ovens.



DR. FRIEDRICH W. C. SCHNIEWIND

- 976,930, Coke Oven and Heating Arrangement therefor.
 976,931, Coke Oven and Door therefor.
 976,932, Car Construction.
 976,933, Apparatus for Draining Gas-pipes.
 976,934, Coke Oven Discharging Apparatus.
 976,935, Coke Oven and Door therefor.

From 1895 up to the present time plants were installed as follows

COMPANY	INSTALLMENTS	LOCATION	OVENS	USE OF COKE	USE OF SURPLUS GAS
Cambria Steel Co.	1st	Johnstown, Pa.	60	Blast Furnace	Fuel & Power
Cambria Steel Co.	2nd	Johnstown, Pa.	100	Blast Furnace	Fuel & Power
Cambria Steel Co.	3rd	Johnstown, Pa.	100	Blast Furnace	Fuel & Power
Cambria Steel Co.	4th	Johnstown, Pa.	112	Blast Furnace	Fuel & Power
Pitts. Gas & Coke Co.		Glassport, Pa.	120	Blast & Domestic	Illuminating & Fuel
New Eng. G. & C. Co.		Everett, Mass.	400	Domestic & Locomotive	Illuminating & Fuel
Dominion I. & S. Co.		Sydney, N. S.	400	Blast Furnace	Fuel
Dominion I. & S. Co.		Sydney, N. S.	120	Blast Furnace	Fuel
Hamilton Otto C. Co.		Hamilton, Ohio	50	Foundry & Domestic	Illuminating & Power
Hamilton Otto C. Co.		Hamilton, Ohio	50	Foundry & Domestic	Illuminating & Power
Lackawanna Steel Co.		Lebanon, Pa.	232	Blast Furnace	Fuel
Lackawanna Steel Co.		Buffalo, N. Y.	564	Blast Furnace	Fuel
S. Jersey Gas, El. & Traction Co.	1st	Camden, N. J.	100	Foundry & Domestic	Illuminating & Power
S. Jersey Gas, El. & Traction Co.	2nd	Camden, N. J.	50	Foundry & Domestic	Illuminating & Power
Maryland Steel Co.		Sparrow's Pt., Md.	200	Blast Furnace	Illuminating
Michigan Alkali Co.	1st	Wyandotte, Mich.	15	Lime Kilns	Fuel
Michigan Alkali Co.	2nd	Wyandotte, Mich.	15	Lime Kilns	Fuel
Sharon Coke Co.		S. Sharon, Pa.	212	Blast Furnace	Fuel
Zenith Furnace Co.		Duluth, Minn.	50	Blast Furnace	Illuminating
*Citizens Gas Co.	1st	Indianapolis, Ind.	50	Metallurgy & Domestic	Illuminating
*Northwestern I. Co.		Mayville, Wis.	36	Blast Furnace	

Dr. Schniewind's latest patents bearing upon a large vertical oven had not, at the time of his death, been carried out in actual practice. The important considerations in connection with this patent are the possibility of coking a larger tonnage of coal at a single charge, and the possible adaptation of this oven for gasifying coals which do not cake, this being accomplished by the bottom discharge.

Dr. Schniewind was a member of the following societies: American Gas Institute, Deutscher Verein fuer Gas u. Wassera-fachmaenner, National Commercial Gas Association, Illuminating Engineering Society, Franklin Institute, Verein Deutscher Ingenieure, Deutsche Chemische Gesellschaft, Verein Deutscher Eisenhuettenleute, Society of Chemical Industry,

American Institute of Mining Engineers, American Society of Testing Materials, Technischer Verein von New York, Verein Deutscher Chemiker, American Association for Advancement of Science, American Chemical Society, National Association of German American Technologists, Deutsche Beleuchtungs-technische Gesellschaft, American Institute of Chemical Engineers, Inventors' Guild, Engineers' Club, Chemists' Club, Deutscher Verein, Whitehall Club, Englewood Club, Germanistic

Society, American Forestry Association, American Museum of Natural History, New York Zoological Society, National Geographical Society, Weinheimer Alter Herren Vereinigung, Deutsche Gesellschaft für Stadt New York.

To those whose privilege it was to know him personally, Dr. Schniewind's untimely death brings a deep sense of loss. No one could become acquainted with him without learning to admire the breadth, generosity and sincere kindness of his nature. His charities to his less fortunate compatriots were incessant. His work did much for the progress of the coke and gas industries and if spared he would have done much more. He is survived by a wife and two sons.

T. J. PARKER.

NOTES AND CORRESPONDENCE

LEAD POISONING

Editor of the Journal of Industrial and Engineering Chemistry:

I wish to say a few words regarding the sensational statements that have appeared lately in the press concerning the poisonous effects of white lead on workmen. It is very true that lead injected or absorbed in any form into the system produces plumbism, but the matter is not as serious as sensational newspaper writers have made it. All this talk about putty powder poisoning men in glass polishing factories is practically untrue, for putty powder happens to be tin oxide or a mixture of tin oxide and precipitated barium sulfate. The use of lead compounds in the preparation of wall papers is just as ridiculous as the arsenical poisoning which was supposed to have injured so many operatives who used green pigments for printing wall paper designs. It turned out—of course, afterwards—that the green pigments were chrome pigments, and the percentage of arsenic contained in the aniline dyes was so minute that even if they had dusted off it is a question whether they would have done any harm, for the pigments which are printed on wall paper are never released from their base.

The precautions that are taken in the white lead factories in the United States are so great that the plumbism which re-

sults is due to a large extent to the carelessness of the workmen themselves. As far as my personal experience goes, it is the hardest thing in the world for us to educate illiterate workmen that they must wash their hands before they eat, and the State is now distributing circulars printed in various languages notifying workmen that it is illegal for an employer or an employee to permit food to be consumed where these materials are manufactured. We are well aware that the transportation of high explosives is exceedingly dangerous. There have been some frightful holocausts resulting from explosions in transit, and yet it is safe to say that any civilized country would go back untold and countless years if laws were enacted prohibiting the transportation of explosives, for coal, metals and minerals would lie practically untouched in the ground; and the only safeguard is, that, knowing that the materials are necessary for the excavation of the riches of the earth, due care should be taken in the transportation of explosives. Practically the same is true in the manufacture of any hazardous material, and therefore sensational and irresponsible statements pertaining to the manufacture of any chemical, whether it be lead or nitroglycerine, are to be decried.

MAXIMILIAN TOCH

320 FIFTH AVE.
NEW YORK

THE AMERICAN ALCOHOL INSOLUBLE TEST FOR SHELLAC¹

Shellac contains, in addition to the resin and wax, impurities such as sand, orpiment, charcoal, fibers, etc., which may amount to several per cent. Inasmuch as these materials are insoluble in dilute alkalis and in alcohol and are of no value to users of shellac, the determination of their amount is a matter of some importance. This has been recognized by the U. S. government in specifications for "orange gum shellac" with the requirement that the insoluble residue after treatment with hot 95 per cent alcohol shall not exceed $1\frac{3}{4}$ to 3 per cent depending on the grade of shellac.

Grain lac, which is prepared from stick lac by crushing, washing and drying, may contain insect cells, sand, fragments of wood, etc., amounting to 3 per cent and upwards of alcohol insoluble matter. Grain lac brought into the United States is sold with a guarantee on alcohol insoluble matter as determined by analysis and it is therefore necessary to publish a method which may be depended upon to yield concordant results in the hands of various chemists. Considerable difficulty has been experienced with the usual forms of extraction apparatus on account of the wax present in shellac amounting to about 5 per cent. Shellac wax is soluble in boiling hot alcohol, but separates when cold and clogs the paper. A form of apparatus permitting continuous extraction with very hot alcohol is required.

A committee consisting of the undersigned, at a meeting in the Chemists' Club, New York, Feb. 21, 1913, agreed upon the following method for the estimation of the proportion of alcohol insoluble matter in stick-lac, grain or seed-lac, and shellac in its various forms. This agreement was reached after several months' work by each of the above named gentlemen upon a standard sample of grain-lac. Several grades of methyl alcohol, as well as ethyl alcohol, and various types of apparatus were used, with the result that the apparatus described in the accompanying drawing, and methyl alcohol containing not more than 0.5 of one per cent of water and impurities, were adopted as the apparatus and solvent most likely to give uniform results in the hands of various operators.

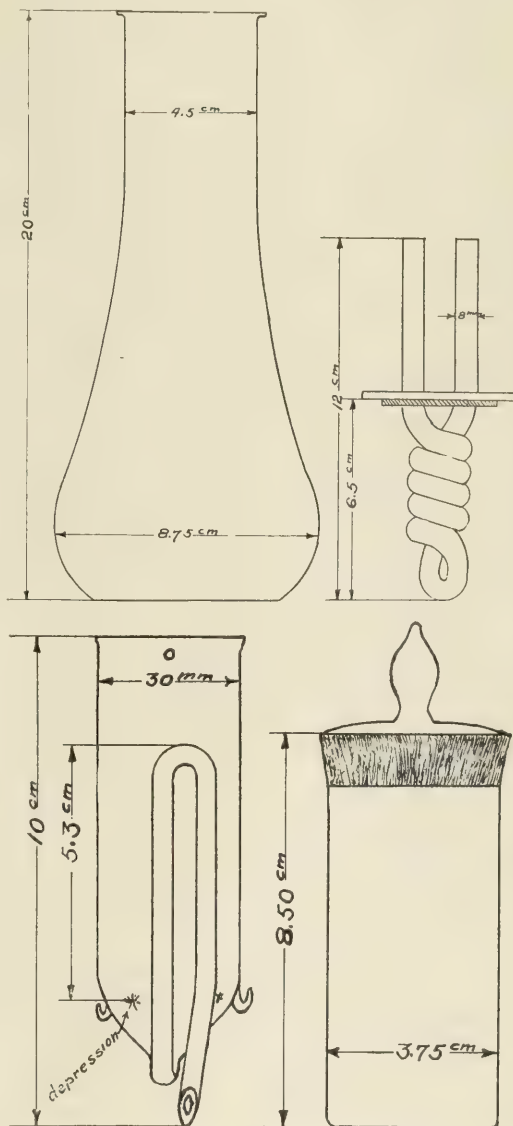
The method has been approved by the United States Shellac Association.

The separation of the soluble from the insoluble portion of the lac is made by extracting approximately 5 grams of the lac in a paper cartridge which is held in a tube provided with a syphon as in the Knoefler extraction apparatus and heated by the vapors of the alcohol which pass around the tube and are then condensed by a return condenser to fall as liquid upon the shellac to be extracted. The syphon tube should be slightly larger than the cartridge which should be supported so that it does not rest directly on the bottom.

The most convenient apparatus for carrying out the process is illustrated in the drawing. It consists of a wide-necked flask in which is suspended a metal return condenser from the lower part of which is hung a syphon tube of the Knoefler type. A Schleicher & Schuell extraction cartridge, No. 603, 26 mm. in diameter by 60 mm. high, is used in a syphon tube of such a size that the top of the cartridge is just above the upper curve of the syphon, the paper thimble being cut down if necessary. It is supported on three indentations in the glass so that there is a little space underneath and around the cartridge to allow of a free flow of liquid. To insure the complete extraction of all matters soluble in alcohol in the cartridge itself it should be thoroughly extracted with 99 $\frac{1}{2}$ per cent methyl alcohol before use. It is then placed in a glass-stoppered weighing bottle and dried to constant weight in an air bath at 100° C. A sample of approximately 5 grams of the pulverized lac is placed in the cartridge which is then transferred to the extraction apparatus. The cartridge is filled with cold alcohol of the character described

to a point just below the upper curve in the syphon. The cold alcohol is allowed to act upon the lac for an hour before the extraction commences.

During the extraction the alcohol is kept boiling briskly. The extraction is stopped one hour after the alcohol in the syphon tube has become colorless. The extraction should be started in the morning and carried along continuously until finished on the same day. The cartridge is after extraction placed in the



APPARATUS APPROVED BY U. S. SHELLAC IMPORTERS' ASSOCIATION FOR THE AMERICAN ALCOHOL INSOLUBLE TEST

weighing bottle, dried to constant weight at 100° C. and the whole weighed.

The weight thus obtained of the residue insoluble in the alcohol divided by the weight of the sample and this quotient multiplied by one hundred is the per cent of alcohol insoluble matter in the lac.

¹ Report of Committee of the U. S. Shellac Importers' Association.

In some quarters a similar test is known as the "refraction" of the lac.

NOTES. It will be noted that there are three depressions in the lower part of the glass extraction thimble to hold the cartridge above the bottom. This is very necessary for the reason that during the early part of the extraction a very free flow must be maintained to prevent the blocking of the syphon with the wax, which though readily soluble in hot alcohol is with difficulty soluble in cold. The object in filling the cartridge with cold alcohol before starting the extraction proper is to allow the resin and some of the wax to dissolve at a low temperature. If the higher temperature of the boiling alcohol were immediately applied it would fuse the resin into a lump and render the extraction difficult. The first few drops of distilled alcohol which fall into the cartridge will cause the extract to syphon over, thus eliminating the bulk of the resin at the start.

If the extraction is continued much longer than the hour limit set above, substances other than shellac which are present will slowly dissolve though their complete extraction may require days.

The total amount of alcohol is not important, but it should be noted that for convenience the alcohol should be of a depth in the flask which will not quite reach the tip of the syphon tube.

The apparatus shown in the drawing may be obtained from Eimer & Amend, New York.

Signed: C. T. BRAGG, *Chairman*, Director of Laboratories, Berry Bros., Detroit.

GEORGE E. ASHBY, of John R. Anderson & Co., New York.

A. C. LANGMUIR, Works Manager, Marx & Rawolle, New York.

PARKER C. McILHINEY, Consulting Chemist, New York.

JOHN W. PAISLEY, Chemist, Rogers & Pyatt, New York.

Approved: H. S. CHATFIELD, *Secretary* United States Shellac Importers' Association.

PRODUCTION OF CAMPHOR IN JAPAN

Consul General Thomas Sammons, of Yokohama, reports that Japanese statistical authorities at Tokyo place the production of camphor in Japan, including Formosa, at 6,600,000 pounds. Assuming that the world's production of camphor amounts to 12,000,000 pounds, Japan is credited with producing over one-half of the world's supply. Formosa is represented by 4,600,000 pounds, and Shikoku and Kyushu by 2,000,000 pounds. It is predicted that the policy of the Japanese Government camphor monopoly may result in the stimulation of the artificial camphor industry, the current price being \$36.50 per catty of 133 pounds for class B coarse camphor.

The Tokyo authorities place the Chinese camphor production at 1,300,000 pounds, and consider the industry in China to be in its infancy. They believe that by forest protection in China the industry could be made very profitable and the output increased. They also indicate that an active rival of the Japanese camphor industry may result from the development of the camphor afforestation in Borneo and Sumatra, where foreigners are extensively interested. However, in most instances the camphor trees in Borneo and Sumatra will not be ready for use for a number of years.

MINERAL PRODUCTION OF CANADA

The Preliminary Report of the Canadian Department of Mines furnishes preliminary figures (subject to revision) of the total value of the mineral production in Canada during 1912 as \$133,127,489. Compared with 1911, this production shows an increase of \$29,906,495, or nearly 29 per cent. A substantial rise in price for most metals during the year had an important

bearing on the year's operations and the increased value of the output.

MINERALS AND MINERALS	1911		1912	
	Quantity	Value	Quantity	Value
Copper, pounds.....	85,648,011	\$ 6,886,998	77,775,600	\$12,709,311
Gold, ounces.....	473,159	9,781,077	607,609	12,559,433
Pig iron, tons.....	917,535	12,307,125	1,014,587	14,380,999
Lead, pounds.....	23,784,969	827,717	35,763,476	1,597,533
Nickel, pounds.....	34,098,744	10,229,623	44,841,542	13,187,460
Silver, ounces.....	32,559,044	17,355,272	31,931,710	19,127,686
Other metallic products.....		411,332		982,566
Total.....		57,799,144		75,274,102
Less pig iron credited to imported ores, tons.....	875,349	11,693,721	978,232	14,100,113
Total metallic.....		46,105,423		61,173,989
Asbestos and asbestic, tons.....	127,414	2,943,108	131,260	2,979,184
Coal, tons.....	11,323,388	26,467,646	14,699,953	36,440,289
Gypsum, tons.....	518,383	993,394	576,498	1,320,888
Natural gas.....		1,917,678		2,311,126
Petroleum, barrels.....	291,092	357,073	243,336	445,086
Salt, tons.....	91,582	443,004	95,053	459,582
Cement, barrels.....	5,692,915	7,644,537	7,120,787	9,083,216
Clay products.....		8,359,933		9,343,321
Lime, bushels.....	7,533,525	1,517,599	7,992,234	1,717,771
Stone.....		4,328,757		4,673,831
Other nonmetallic products.....		2,142,842		3,364,017
Total nonmetallic.....		57,115,571		71,949,509
Grand total.....		103,220,994		133,127,489

CEMENT PRODUCTION AND CONSUMPTION

The data of production of cement are of particular interest in view of the widespread demand for this material. Statistically the important features of the industry during 1912 were increases of over 26 per cent in the Canadian output, 116 per cent in imports, and 34 per cent in the total consumption. Canadian mills supplied 83.2 per cent of the consumption as against 90 per cent in 1911. The total quantity of Portland cement, including slag cement and natural Portland, made in 1912, was 7,169,184 barrels. The quantity of Canadian cement sold or used was 7,120,787 barrels, valued at the mills at \$9,083,216, or an average of \$1.27 per barrel. The total imports of cement were 5,020,446 hundredweight, equivalent to 1,434,413 barrels of 350 pounds each, and valued at \$1,969,529, or an average of \$1.37 per barrel. Detailed statistics of production during the past four years are as follows:

	1909	1910	1911	1912
Portland cement sold, barrels.....	4,067,709	4,753,975	5,692,915	7,120,787
Portland cement manufactured, barrels.....	4,146,708	4,396,282	5,677,539	7,169,184
Stock on hand, Jan. 1, barrels.....	1,098,239	1,189,731	918,965	904,165
Stock on hand Dec. 31, barrels.....	1,177,238	832,038	903,589	952,562
Value of cement sold.....	\$5,345,802	\$6,412,215	\$7,644,537	\$9,083,216
Wages paid.....	\$1,266,128	\$1,409,715	\$2,103,838	\$2,591,099
Men employed.....	2,498	2,220	3,010	3,379

Canada's imports of cement in 1912 included 130,580 barrels from Great Britain, 1,280,958 barrels from the United States, 6,107 barrels from Belgium, 15,857 barrels from Hongkong, and 911 barrels from other countries.

WATERS OF THE BREITENBUSH HOT SPRINGS, OREGON—A CORRECTION

In the article of the above title, *THIS JOURNAL*, 5, 300, the first six lines in the second column below the table should precede the matter in the same column above the table.

WALTON VAN WINKLE

BOOK REVIEWS

Utilization of Atmospheric Nitrogen. By THOMAS H. NORTON. Department of Commerce and Labor, Bureau of Manufactures. Special Agents Series No. 52. Government Printing Office, Washington, D. C., 1912. Price, \$0.15.

This 8vo volume contains 176 pages of subject matter, a bibliography of two pages, and 5 illustrations. The following subjects are considered: The Present Supply of Nitrogen; available Sources of Combined Nitrogen; Synthetic Production of Ammonia; Synthesis of Nitric Acid from Atmospheric Nitrogen and Oxygen; Synthesis of Hydrocyanic Acid and the Cyanides from Atmospheric Nitrogen; Atmospheric Nitrogen in the Form of Nitrides; Calcium Cyanamide from Atmospheric Nitrogen; Coal Waste and Peat as Sources of Ammonia. In the discussion of processes, the various methods are described and accounts of the plants engaged in the industry are given.

Since the United States now spends over \$32,000,000 abroad for nitrogen in its various combinations, Mr. Norton's report could prove of great interest to the agriculturalist and chemist. Cyanamide is now being manufactured at two points on American soil; it is proposed to utilize the water-power of Maine in the synthetic production of nitric acid from the atmosphere; and the United States is regarded as one of the countries most favored for the establishment of the manufacture of aluminum nitride. Certainly, as Mr. Norton concludes, "it can be regarded as beyond doubt that the present achievements of applied chemistry in this field render it possible for American industry and American agriculture to face the threatened exhaustion of the nitrate deposits of Chile and the demands attendant upon a rapidly growing population without any feeling of apprehension."

W. A. HAMOR.

Proceedings of the American Gas Institute. Sixth Annual Meeting, October 18, 19, and 20, 1911, St. Louis, Mo. 2 Volumes. Published by the Institute, 29 West 39th Street, New York.

The work of this Institute has increased so much that it is now found necessary to publish the Proceedings in two volumes of about 600 pages each. These volumes consist of the address of the President, reports upon special subjects in connection with gas industry such as calorimetry, cast iron pipes, photometry, together with a series of papers covering the entire industry.

At the end of the second volume is a series of three most important reports by the International Committee on Photometry held at Zurich, and published under the auspices of the Société Technique de L'Industrie Du Gaz en France. These comprise papers by such men as Dr. H. Bunte, of Karlsruhe, Sainte-Claire Deville, Messrs. Charles Carpenter and Helps, of England, M. Bohm, T. H. Vautier, Dr. Kruss, of Hamburg, Dr. Emil Liebenthal, Mr. C. C. Paterson, of the National Physical Laboratory of England, M. Perot and M. Janet, of Paris; also Laporte, Dr. Hugh Strache, Prof. A. Blondel and others, comprising one of the most extensive and exhaustive reports upon photometry that has been published for many years.

In the Proceedings of the Institute we note articles on the various commercial details of the gas business together with papers upon Condensation, the Manufacture of Sulfate of Ammonia, the Electrolysis of Underground Pipes, the Flow of Gas in Mains, the Distribution of Gas under High Pressure, a number of articles on Tar and its Products and also several important papers on Coke-Oven plants including also the very important lecture by Professor W. A. Bone on Surface Combustion.

In the report of the Committee on Wrinkles and the Bureau of Information are found many ingenious contrivances for use in and around a gas works.

Among the most important contributions is the one upon condensation with special reference to Water Gas. Here we find the work of such men as Mr. L. E. Worthing, President I. C. Copley, Mr. W. H. Gartley, Mr. H. L. Doherty, Capt. W. E. McKay and Mr. J. B. Klumpp.

There are three important articles on the manufacture of Ammonia Sulfate by Messrs. W. H. McIlravy, C. G. Atwater and Howell Fisher; and a paper on the Electrolysis of Underground Pipes by Burton C. McCollum, followed by a discussion by Messrs. W. H. Fulweiler, F. N. Morton, Carl Graf, J. D. von Maur, A. S. Miller and others.

There is an excellent paper on the Flow of Gas in Mains by Mr. J. W. Batten. This paper gives some good work done in this field of investigation using the Pitot tube. The paper was discussed by Mr. O. H. Fogg, Mr. Fulweiler and Mr. Griswold.

Another excellent paper was by Mr. A. D. Whitaker on "Tar and its Products," in which the author takes a very wide range of the subject and describes the use of tar for creosoting, also for road binders, paving, and the production of creosote, tar paint, roofing pitch and products of that character. This paper is well illustrated and may be considered one of the best that has been published for some time. The working results in this paper are very well described and illustrated.

Mr. Warren S. Blauvelt gives an excellent paper on the development of a By-Product Coke-Oven gas plant, which is one of the best descriptions published of the Semet-Solvay process. It is illustrated with some excellent drawings and plans showing the actual working processes. In this connection also we have a paper by Mr. Carrol Miller on the Vertical Retorts used by the Providence Gas Company. This too is one of the best papers of its kind giving a great many results with figures of high technical value.

We also have another paper by Mr. W. G. Africa on Vertical Retorts at Manchester, N. H., giving working results in this case also. Both these papers were discussed by Messrs. Macbeth, Fulweiler, Forstall, Hartman, Doherty, Captain McKay, R. M. Searle and others.

In a review of this character it is practically impossible to give any details showing the value of these papers. All that can be done is to indicate the line of work pursued by the authors. The members of this society are among the most active and progressive men in the gas industry in the United States, and a large number of them write in a very admirable manner and give very careful descriptions of the work they are engaged in. It is indeed very agreeable to note the care with which most of these articles are presented and we think that the society is to be congratulated on the number of men who can write good papers for these meetings.

The volumes are full of valuable illustrations in the shape of reproductions of photographs, together with plans and working drawings illustrating the papers presented. In the Wrinkle Department are a large number of devices carefully sketched, and in many cases photographed that must prove invaluable to the gas engineer. Both these volumes should be found in the library of every gas engineer in the United States who wants to consider himself anywhere near the front rank in his profession.

ARTHUR H. ELLIOT

Treatise on General and Industrial Inorganic Chemistry. By DR. ETTORE MOLINARI. Third revised and amplified Italian edition, translated into English by Dr. Ernest Feilmann. 8vo., pp. 704. P. Blakiston's Son & Co., Philadelphia. Price, \$6.00.

This is a valuable work on the subjects it treats. The reviewer if of a critical temperament is at the beginning somewhat disarmed by the translator's preface in which he states "in this translation the original text has been adhered to as faithfully as possible even where the views or explanations of the author are not such as would meet with unqualified acceptance by all chemists." But what shall we say of the translator who, in his desire to express too literally the text, makes some curious mistakes. These on the whole are very minor, as for instance in the Leblanc Soda Process he states that "the coal used should contain a little ash," whereas he should say "but little ash," as its silica and alumina are injurious to the process for obvious reasons—and in describing the properties of hydrogen, it is stated that it may be poured from one vessel to another—the translator intended to say transferred from one vessel to another by ascension.

The author is to be commended for his knowledge as well as the scholarly manner in which he has expressed himself. Much valuable information is given in footnotes, in fact so important is it in many cases that it could with advantage be incorporated in the text. He properly claims that the work will enable the young chemist to prepare himself for practical activity. The reviewer will go further than this: it is a book which should be in the library of the chemical manufacturer, not alone for the theory and practice of chemistry outlined, but also for its valuable statistical matter; with all, it is a most readable book and well worth the price. Its text is up-to-date and a fair résumé is given of the principal products of industrial chemistry. It does not read like a compilation, as so many of our books on the subject do, but shows an intimate knowledge by the author of his profession.

Of course, no treatise on the subject can be perfect. There are some omissions which might well be incorporated, as for instance in speaking of the Leblanc Process of Soda manufacture he states "when the operation (of black balling) is almost finished, 6 to 7 per cent. further of sodium sulfate and a little limestone are added," but does not say why. It is, of course, to destroy cyanides derived from the nitrogen of the coal used.

Some statements are made which if not incorrect theoretically are misleading, as, for instance, in speaking on the regeneration of sulfur from tank waste by the Chance-Claus method he states that the hydrogen sulfide is burnt with an insufficient quantity of air. This is hardly correct, as the reaction is brought about by the catalytic action of ferric oxide or rather hematite heated to the necessary temperature: this temperature, a very critical point, being then maintained by the reaction, if a carefully adjusted amount of air is mixed with the hydrogen sulfide.

In writing on potable water the footnote states that there are in the United States 400,000 cases of typhus per annum, with 35,000 deaths, due to drinking polluted water. The American reader will of course understand that typhoid is meant: in England and the Continent they often confound these terms in speaking of the disease. In the examination of drinking-water it is stated that it is sometimes necessary to make a bacteriological examination. This is always necessary. Again, the author says that the dry residue from potable water should show no blackening or volatility on incineration. It is unnecessary to say that very few waters will stand this test.

In writing of sulfuric acid in a footnote he states "acid free from arsenic is obtained by diluting fuming sulfuric acid which is free from impurities (injurious)" and on the same page that "in order to obtain sulfuric acid free from arsenic, sulfur or brimstone must be used." Both statements are correct, if in

the former case, the Badische Herreshoff contact process is used.

Very interesting are the articles on the oxides of nitrogen, particularly NO, N₂O, NO₂, N₂O₄, and HNO₃. In writing on N₂O, NO₂ and N₂O₄, more especially where they are found dissolved in commercial nitric acid before purification, the author leaves us in doubt whether in his opinion the chief impurity is N₂O or N₂O₄, or both, and if both, in what proportions do they relatively exist in it. On pages 336 to 343 where they are mentioned in this connection he uses both forms of expression indiscriminately. As for NO₂ and N₂O₄, this may be permissible as they are interconvertible, as may be deduced from their respective vapor densities, but with N₂O₃ it is not so. The manufacturing chemists generally regard the lower oxide as being N₂O₃, if not entirely at least in great part, whereas the purchaser regards and expresses it as N₂O₄. The importance to the manufacturer of how they are denominated can be understood when we know that the accepted method for their determination is by potassium permanganate, and that it requires nearly 2½ times as much permanganate to equal the same quantity of N as N₂O₄, as it would of N₂O₃, since N₂O₃ × 2.421 = N₂O₄. This problem is worthy of careful research.

In consulting the table on nitric acid where degrees Beaumé are used the American reader must remember that the modulus used in Europe for converting degrees B. into sp. gr. is 144, whereas in the U. S. it is 145.

Thus, in Europe Beaumé = 144 — 144/sp. gr.

in U. S. Beaumé = 145 — 145/sp. gr.

The same observation applies to all Beaumé scales given.

In speaking of the production of copper matte in cupolas, it is stated that the slag which separates in the furnaces contains up to 1 per cent of copper. In American practice anything over 0.35 per cent would be considered very bad work.

The metallurgy of the important metal nickel is incompletely described—undue prominence is given to the Mond process, which is not used in this country.

Under calcium phosphate, chemical manures and superphosphates, a good description of these products as applied to chemical fertilizers is given and their method of manufacture. The American manufacturer has, however, little to learn from it that is new, as our practice is more advanced than that abroad. The statistics giving the amount of capital invested in the industry in this country are very much understated, as is the production of superphosphate.

Under glass manufacture, little is said descriptive of tank furnaces, which are so largely used in this country for window glass especially. Some of the statistical information under this head could with profit be omitted and its space given to an account of up-to-date tank furnaces. This more particularly as the U. S. manufacture nearly as much glass as all the rest of the world, more than half of which is melted in tank furnaces; otherwise the article is well written and instructive.

A feature to be noted is that of prices of chemical products. In the majority of instances these are fairly correct for the countries mentioned, but here again the reader must be reminded that they are based on the prices paid for raw material, labor, etc., which are subject to wide fluctuations, as, for instance, in the case of nitric acid, its prices are evidently based on a price of, say, \$1.90 per 100 lbs. for nitrate of soda, whereas at present its price has risen to \$2.60 or over. The same may be said of sulfate of copper, the metal being now much higher than its price was when given in the book.

The manufacturing costs given are in some cases very wide of the truth, at least as far as U. S. is concerned.

The indexing is to be commended as it is very complete.

Lastly, we must bear in mind that the book was written chiefly for the information of the European reader.

T. J. PARKER

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York

Alkaloids, Exact Quantitative Determination of, The Methods of. By A. V. KORZANSKI. 8vo. Price, \$1.00. Gebroeder Borntraeger, Berlin. (German.)

Alkaloids, The Plant. By THOMAS A. HENRY. 8vo. Price, \$4.50. J. & A. Churchill, London.

Ammonia, The Oxidation of, to Nitric and Nitrous Acid. By E. DONATH AND A. INDRÁ. 8vo. Ferdinand Enke, Stuttgart. (German.)

Areometry, Handbook of. By J. DOMKE AND E. REIMERDES. 8vo., pp. 235. Price, \$3.25. Julius J. Springer, Berlin. (German.)

Caoutchouc and Gutta-Percha Resins. By G. HILLEN. L. 8vo., pp. 95. Price, \$0.75. M. Drechsel, Bern. (German.)

Chocolate Manufacture. By P. ZIPPERER. 3rd edition. L. 8vo., pp. 349. Price, \$2.50. M. Krayn, Berlin. (German.)

Cotton Manufacturing Industry of the United States. By M. T. COPELAND. 8vo. Price, \$2.00. Harvard University, Cambridge.

Dyes, Subsidiary, in the Permitted Food Colors, Quantitative Separation and Determination of. By WALTER E. MATHEWSON. 8vo., pp. 4. U. S. Dept. of Agriculture, Bureau of Chemistry Circular No. 113.

Dye-stuffs, Identification of Small Amounts of, by Oxidation with Bromin. By WALTER E. MATHEWSON. 8vo., pp. 3. U. S. Dept. of Agriculture, Bureau of Chemistry Circular 114.

Electrochemical Practice. By ERICH MUELLER. 8vo. Price, \$2.00. Theodor Steinkopff, Dresden. (German.)

Electrolytic Decomposition of Alkali Chlorides with Solid Cathode Metals. Part II. By J. BILLITER. 8vo. Price, \$2.25. Wilhelm Knapp, Halle. (German.)

Fertilizers, Utilization of Acid and Basic Slags in the Manufacture of. By WILLIAM H. WAGGAMAN. 8vo., pp. 18. U. S. Dept. of Agriculture, Bureau of Soils Bulletin 95.

Flour Manufacture, Processes of. By P. A. AMOS. 8vo., pp. 280. Price, \$1.50. Longmans, Green & Co., New York.

Gas Power. By C. F. HIRSHFELD AND T. C. ULBRICHT. 8vo., pp. 209. Price, \$1.25. John Wiley & Sons, New York.

Industry, Elements of Chemical. By J. GROSSMANN. 2nd edition 8vo., pp. 152. Price, \$1.00. Chas. Griffin & Co., London.

Insecticides, Fungicides and Weed Killers. (Translation.) By E. BOURCARD. D. 8vo., pp. 450. Price, \$4.50. Scott, Greenwood & Son, London.

Iron and Steel, Manufacture of. By H. R. HEARSON. Cr. 8vo., pp. 104. Price, \$1.25. Spon & Chamberlain, New York.

Liquid Air, Oxygen and Nitrogen. (Translation.) By GEORGES CLAUDE AND H. E. P. COTTELL. 8vo. Price, \$4.50. J. & A. Churchill, London.

Metallic Alloys, Their Structure and Constitution. By G. H. GULLIVER. 2nd edition. 8vo., pp. 409. Price, \$2.75. Chas. Griffin & Co., London.

Mineral Kingdom, The. By REINHARD BRAUNS AND L. J. SPENCER. Demy 4vo. Price, \$17.50. J. B. Lippincott Co., Philadelphia.

Microscopic Determination of Soil-Forming Minerals. By W. J. MCCAUGHEY AND WILLIAM H. FRY. 8vo., pp. 100. U. S. Dept. of Agriculture, Bureau of Soils Bulletin 91.

Organic Chemistry. By HOWARD D. HASKINS. 8vo., pp. 430. Price, \$2.25. Chapman & Hall, London.

Organic Compounds, Qualitative Determination of. By J. W. SHEPHERD. 8vo., pp. 348. Price, \$1.75. W. B. Clive, London.

Patent and Trade Mark Laws of all Countries. By BRUNO ALEXANDER-KATZ. Vol. 2. 8vo. Price, \$3.00. W. Rothschild, Berlin. (German.)

Petroleum, Scientific Basis of Treatment of. By L. GURWITSCH. 8vo., pp. 275. Price, \$2.50. Julius Springer, Berlin. (German.)

Pyrites in Canada: Its Occurrence, Exploitation, Dressing and Uses. By ALFRED W. G. WILSON. 8vo., pp. 202. Canada Dept. of Mines, Publication No. 167.

Sampling and Testing, Notes on. ANONYMOUS. 8vo., pp. 94. Price, \$0.50. Marsden & Co., Manchester, England.

Sugar, The Manufacture of. By D. SIDERSKY. 8vo., pp. 356. Price, \$1.00. Octave Doin & Fils, Paris. (French.)

Sugar Manufacture. By S. FREILER. 8vo. Price, \$1.25. Alfred Hoelder, Vienna. (German.)

Sulfuric Acid and Alkali, The Manufacture of. By GEORGE LUNGE. 3rd edition. 8vo., pp. 1666. Price \$16.00. Gurney & Jackson, London.

Tanning Methods, Modern. JOSEF JETEMAR. 8vo. Price, \$1.50. W. Hartleben, Leipzig. (German.)

Technology, Chemical, of Organic Compounds. By R. O. HERZOG. 8vo. pp. 732. Price, \$5.50. Carl Winter, Heidelberg. (German.)

Textile Fibres. By J. MERRITT MATTHEWS. 3rd edition. 8vo., pp. 630. Price, \$4.00. John Wiley & Sons, New York.

Textiles, The Chemistry and Practice of Finishing. By BEAN

AND MCCLEARY. Vol. 2. New American edition. 8vo. Price, \$15.00. Lord & Nangle Co., Boston.

Waters and Water Supplies, The Examination of. By J. C. THRESH. 2nd edition. 8vo. Price, \$4.50. J. & A. Churchill, London.

RECENT JOURNAL ARTICLES

Boiler Compounds and Scale Prevention. By L. KUNZ. *Pure Products*, Vol. 9, 1913, No. 3, pp. 107-111.

Cellulose, Studies on. By EDWARD C. PARKER. *Journal of Physical Chemistry*, Vol. 17, 1913, No. 3, pp. 219-229.

Condensing Water Systems, Wheeler-Balcke Cooling Tower for. ANONYMOUS. *Industrial World*, Vol. 47, 1913, No. 13, pp. 378-380.

Electroplating: The Action of Added Substances in Galvanoplastic Lead Baths. By FRANK C. MATHERS AND O. RALPH OVERMAN. *Chemiker Zeitung*, Vol. 37, 1913, No. 34, pp. 341-344.

Engineering Problems in the Brewery Power Plant. By G. J. PATITZ. *Pure Products*, Vol. 9, 1913, No. 3, pp. 123-133.

Ethereal Oils, Adulteration to the Principal, and their Detection. By J. C. SMITH. *Pure Products*, Vol. 9, 1913, No. 4, pp. 192-197.

Fats, Hardened. By MARTIN AUERBACH. *Chemiker Zeitung*, Vol. 37, 1913, No. 30, pp. 297-299.

Fats, The Hydrolysis of the. By J. MARCUSSEN. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 25, pp. 173-176.

Fertilizers: Chemico-Technological Notes on the Preparation and Purification of Fish Powder. By C. KIPPENBERGER. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 21, pp. 154-158.

Foundry, Some Aids to Scientific Management in the. By W. M. CORSE. *Industrial World*, Vol. 47, 1913, No. 17, pp. 322-323.

Fuels, Liquid, Chemical Examination of. By W. HAMILTON PATTERSON. *Journal Society of Chemical Industry*, Vol. 32, 1913, No. 5, pp. 218-220.

Fuel, Oil as an Emergency. By REGINALD TRAUTSCHOLD. *Practical Engineer*, Vol. 17, 1913, No. 6, pp. 304-306.

Heat Economy. By CHARLES R. DARLING. *Chemical Trade Journal*, Vol. 52, 1913, No. 1346, pp. 259-260.

Lacquer, Chinese and Japanese, Notes on the Properties of. By HENRY A. GARDNER. *Paint, Oil & Drug Review*, Vol. 55, 1913, No. 14, pp. 10-11 and 32.

Peroxids and Persalts. By A. S. NEUMARK. *Scientific American Supplement*, Vol. 75, 1913, No. 1942, pp. 182-183.

Power Plant Chemistry. ANONYMOUS. *Practical Engineer*, Vol. 17, 1913, No. 7, 347-350.

Rubbers, Ceara and Rambong, Insoluble Constituents of. By CLAYTON BEADLE AND HENRY P. STEVENS. *India Rubber Journal*, Vol. 45, 1913, No. 7, pp. 5-6.

Rubber Industry, Some Problems of the. By H. E. POTTS. *Oil & Colour Trades Journal*, Vol. 43, 1913, No. 752, pp. 917-972.

Sewage-Treatment Studies at Akron, Ohio. By HARRY B. HOMMON. *Engineering Record*, Vol. 67, 1913, No. 14, pp. 387-390.

Storage Battery, Edison, Some Tests of the. By C. W. BENNETT AND H. N. GILBERT. *Journal of Physical Chemistry*, Vol. 17, 1913, No. 4, pp. 322-330.

Sulfite Pulp, Steps in the Manufacture of. By F. M. WILLIAMS. *Paper*, Vol. 11, 1913, No. 1, 17-20.

Surface Combustion: The "So-called" Flameless Gas Heating. By HENRICH MACKE. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 23, pp. 167-168.

Sugar Laboratory Apparatus and its Use. By R. S. NORRIS. *International Sugar Journal*, Vol. 15, 1913, No. 171, pp. 126-133.

Textile Industry, Water in the. By WILLIAM H. RUTHERFORD. *Textile Colorist*, Vol. 35, 1913, No. 411, pp. 57-59.

Turpentine and Turpentine Substitutes. By F. MALLOW PERKIN. *Oil & Colour Trades Journal*, Vol. 43, 1913, No. 750, pp. 791-794.

Vanadium in Ferro-Vanadium, Determination of. By WM. W. CLARK. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 4, pp. 195-197.

Viscosity of Rubber Solutions, Determination of the Degree of. By J. G. FOL. *India Rubber Journal*, Vol. 45, 1913, No. 12, pp. 18-21.

Water in Cane Molasses, Determination of. By H. PELLET. *International Sugar Journal*, Vol. 15, 1913, No. 171, pp. 117-120.

Water in Food and other Materials, The Direct Determination of, by Distillation. By FRANZ MICHEL. *Chemiker Zeitung*, Vol. 37, 1913, No. 35, pp. 353-355.

Waterproofing Fabrics. ANONYMOUS. *American Wool and Cotton Reporter*, Vol. 27, 1913, No. 13, pp. 394-395.

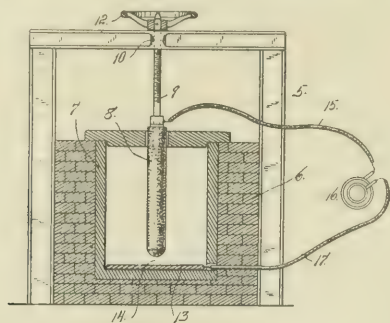
Waterproofing: Impermeable Cotton Goods. By RAFFAELE SAN-SOME. *Textile Manufacturer*, Vol. 39, 1913, No. 459, pp. 96-97.

Wood Pulp Processes, Commercial. The Utilization of Spent Extractive Liquors. By THOMAS J. KEENAN. *Pulp and Paper Magazine of Canada*, Vol. 11, 1913, No. 7, pp. 239-242.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Process of Extracting Aluminum from its Ores. Alan Kiscock, Feb. 11, 1913. U. S. Pat. 1,052,727. A charge is formed consisting of an intimate mixture of any suitable aluminum-bearing material, sufficient carbon to convert the contained aluminum into aluminum carbid, and the required amount of some suitable compound of sulfur to change the aluminum carbid, into aluminum sulfid; or the charge may consist of an intimate mixture of any aluminum-bearing material, sufficient carbon to convert the contained aluminum into aluminum carbid, the



aluminum sulfid to be formed later by heating the aluminum carbid with the required amount of sulfur or some compound of sulfur to change the aluminum carbid to aluminum sulfid. Either of these charges is put into an electric furnace of suitable design to furnish the required heat for the operation. The aluminum compound thus formed is separated from the resulting mass, dissolved, and electrolyzed in a molten bath of alkaline earth chlorides or fluorides and the resulting aluminum drawn off.

Process of Making Nitrogenous Compounds. C. J. Greenstreet, Feb. 11, 1913. U. S. Pat. 1,052,815. Nitrogen is passed over calcium hydrid and carbon heated with or without an alkaline earth compound such as calcium chloride to a temperature above a dull red heat.

Process for the Manufacture of Product from which Red Lead can be Burnt. Georg Jansen, Feb. 11, 1913. U. S. Pat. 1,052,924. A combined jet of steam, carbonic acid gas and acetic acid vapor is injected into molten lead: an impalpable oxidized powder is produced.

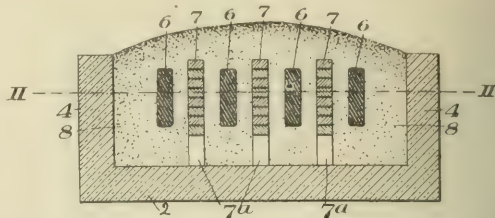
Process of Making Ammonia. Carl Bosch and Alvin Mittasch, Feb. 18, 1913. U. S. Pat. 1,053,951. Gases containing hydrogen and nitrogen are passed over a catalyst containing molybdenum, maintained at a temperature of from about 300° to 900° C. and at a pressure above one hundred atmospheres.

Process of Extracting Vanadium from Carnotite Concentrates. Siegfried Fischer, Feb. 25, 1913. U. S. Pat. 1,054,102. The ore is mixed with alkali hydrate and water to form a paste and this is evaporated to dryness; the insoluble vanadium salts are rendered soluble. In some cases the evaporated product is roasted at low temperature and then leached.

Process for Producing Diastatic Product. Jokichi Takamine, Feb. 25, 1913. U. S. Pat. 1,054,324. The product is produced by sowing an acclimatized diastatic spore upon a culture medium and subjecting it to incubating and antiseptic conditions while securing air contact by keeping the mass in normally continuous agitation.

Method of Silicidizing Articles Containing Carbon. Frank J. Tone, Feb. 25, 1913. U. S. Pat. 1,054,373. The carbon containing articles to be silicidized are assembled in self-supporting piles in a carbon-resistor furnace, the piles being disposed along

Fig. 1.

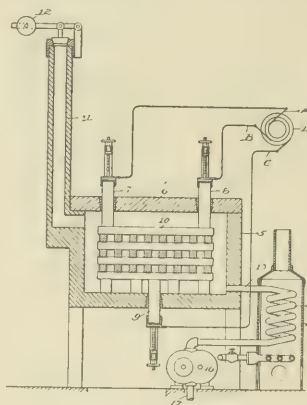


the resistor in position to be heated thereby. The resistor is surrounded by a porous mixture capable of generating silicon-containing vapors, such as a mixture of silica sand, coke and sawdust and a sufficient current is passed through the resistor to silicidize the article under treatment.

Method of Making Ferric Chlorid. H. H. Dow and A. E. Schaefer, Feb. 25, 1913. U. S. Pat. 1,054,400. The ferric chlorid is produced by chlorinating a solution of ferrous chlorid containing solid ferrous chlorid. In some cases the product is treated with chlorin gas. In others the original solution must be acidified with hydrochloric acid.

Method of Revivifying or Restoring Permutit. Gustav Schweikert, Feb. 25, 1913. U. S. Pat. 1,054,460. The mass of permutit to be restored is heated to a temperature of 70° C. or above and treated with a solution of sodium chlorid at such temperature until the mass is revived. The time required varies according to conditions.

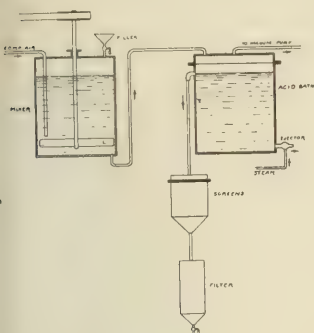
Explosive. Roberto Imperiali, March 4, 1913. U. S. Pat. 1,054,777. The composition consists of metallic tungsten, a tungsten-aluminum or a tungsten-aluminum-silicon alloy and an oxidizing agent.



Cement Steel. G. H. Benjamin, March 4, 1913. U. S. Pat. 1,054,817. The body of iron under treatment is heated to a high temperature out of contact with the air by means of an electric current and a carbon containing gas dissociated by the heat in contact with the iron. The carbon set free combines with the iron to produce the grade of steel required.

Treating Ores. C. Schick, March 11, 1913. U. S. Pat. 1,055,495. In this process there is employed for the purpose of the treatment of sulfid or preferably compound carbonate and sulfate ores, chlorid of benzol or nitro-benzol, each separately or in combination as carriers of the metallic particles.

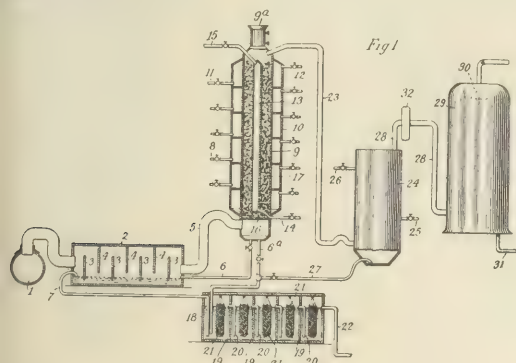
The following is given by way of example of the process: 100 kg. of lead-zinc ore slimes (sulfids) containing 20 per cent of metal are treated alone or mixed with $\frac{1}{2}$ per cent of iron ore with 2 grams of bichlorid of benzol ($C_6H_5Cl_2$) stirred up together in a vessel and passed under pressure into an acid, such as dilute sulfuric, bath $35^\circ C$. There then takes place a complete separation of the crude iron ore and gangue on the one hand and of the sulfid ores on the other,



inasmuch as these ores rise to the surface and the iron ore and the gangue sink. By means of an elevator resistant to acid, or by means of an ejector, the refuse is continually removed from the bottom of the vessel and the floating ores are collected upon strainers. The application of a

vacuum facilitates the process. By the treatment with extraction materials in suitable vessels, the ore slime obtained free from gangue is then extracted, and a product is obtained containing sulfid of lead and sulfid of zinc, which can be easily further treated in suitable smelting furnaces. As the gangue is practically all removed from this product all the zinc ore and lead ore containing silver can be recovered from the liquors through filter apparatus.

Manufacture of Stannic Chlorid. W. F. Doerffinger, March 11, 1913. U. S. Pat. 1,055,617. In this process, anhydrous stannic chlorid is produced by the action of dry chlorin gas, in the presence of stannic chlorid vapor, upon metallic tin, preferably at a temperature of about $35^\circ C$., the heat of reaction being dissipated by cooling surfaces near the point of reaction and the

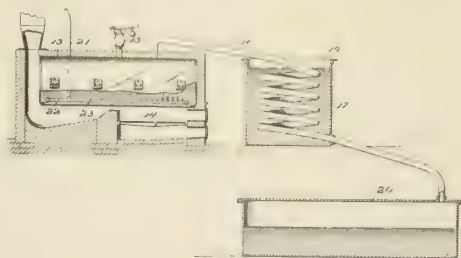


anhydrous chlorid being allowed to drain away as formed. This stannic chlorid, or part of it, is used to saturate the entering chlorin gas with stannic chlorid vapor for the purpose of removing the last trace of water from the chlorin. The presence of water being prejudicial, the use of stannic chlorid vapor is desirable, since it is difficult otherwise to get the chlorin thoroughly dry.

Asphalt Production. W. M. Burton, March 11, 1913. U. S. Pat. 1,055,707. This is a process of producing asphalt by the treatment of the high boiling-point residual portions, and particularly the residue of the distillation of the paraffin group or series of petroleum after the lower boiling-point distillates have been removed.

In carrying out the process a still is charged with the liquid

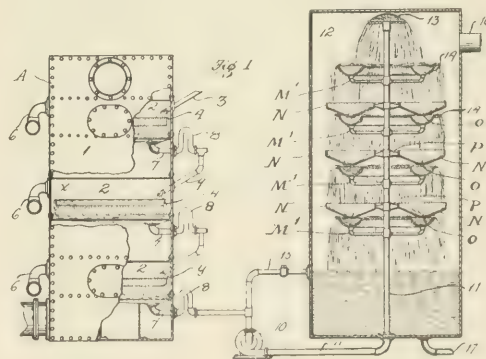
residue which has a boiling point of upward of $500^\circ F$., the charge preferably being of such an amount as to fill the still about half full. Heat is then applied and the pressure held in the still at about 4 to about 5 atmospheres. This causes the liquid to vaporize and to give off its distillates at about 650° to $800^\circ F$.; the distillates are preferably condensed under pressure. This distilling process is continued until the bottom of the still is



red hot, which heating of the bottom is caused by the precipitations of coke therein. The liquid residue is then drawn off from the first still and charged into the second still 13. This liquid residue or tar is limpid, about the consistency of thin syrup, and has a greater specific gravity than water. After the second still 13 is charged, heat is applied thereto from the furnace 14, and steam is supplied through the pipe 21, in order to prevent further cracking. The distilling operation is carried on in the ordinary way, using fire under the still and inert vapor in the still, until from 60 to 70 per cent of the charge has been taken off as a distillate; then the residue remaining in the still 13 is withdrawn and permitted to cool. This residue is asphalt, and has the same chemical and physical characteristics as the natural asphalt.

Extracting Precious Metals from their Ores. S. Williams, March 18, 1913. U. S. Pat. 1,056,311. The ground ore is mixed with a solution of potassium sulfate and superphosphate in water and the mass agitated in the presence of mercury.

Making Asphalt. R. C. Dundas, March 25, 1913. U. S. Pat. 1,056,980. This is a process of making asphalt from crude petroleum, such as is found in California and elsewhere. It is designed to preserve the original asphalt base of the crude petroleum by so distilling the natural oil that no new compounds of the hydrocarbon group are formed.



The natural oil flows continuously in undulatory strata, heating the strata so that the temperature of the same varies from a determined minimum to a determined maximum to drive off the lighter products and gradually inspissate the base. The thick product falls in attenuated streams *in vacuo* thus liberating its nascent vapors.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF APRIL, 1913

ORGANIC CHEMICALS

Acetamide	Lb.	21	@	23
Acetic Acid (28 per cent)	C.	2 00	@	2 15
Acetone (drums)	Lb.	16 1/2	@	17 1/2
Alcohol, denatured (180 proof)	Gal.	37	@	39
Alcohol, grain (185 proof)	Gal.	2 50	@	2 55
Alcohol, wood (95 per cent)	Gal.	49	@	52
Amyl Acetate	Gal.	2 35	@	2 55
Aniline Oil	Lb.	10 1/8	@	10 5/8
Benzene Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal.	21	@	23
Camphor (refined in bulk)	Lb.	42 1/2	@	44
Carbolic Acid (drums)	Lb.	13	@	15
Carbon Bisulfide	Lb.	6 1/2	@	8
Carbon Tetrachloride (drums)	Lb.	8 1/4	@	8 3/4
Chloroform	Lb.	25	@	35
Citric Acid (domestic), crystals	Lb.	40	@	40 1/2
Dextrine (corn)	C.	2 85	/	3 50
Dextrine (imported potato)	Lb.	6	@	7
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite)	Lb.	19 1/2	@	20
Oxalic Acid	Lb.	8 1/4	@	8 1/2
Pyrogallie Acid (bulk)	Lb.	1 20	@	1 40
Salicylic Acid	Lb.	29	@	31
Starch (cassava)	Lb.	3 1/4	@	4
Starch (corn)	C.	2 02	/	2 50
Starch (potato)	Lb.	4 1/4	@	5
Starch (rice)	Lb.	8	@	9
Starch (sago)	Lb.	2 3/8	@	2 3/4
Starch (wheat)	Lb.	5	@	6
Tannic Acid (commercial)	Lb.	35	@	35 1/2
Tartaric Acid, crystals	Lb.	30 1/4	@	31

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7 3/4	@	8
Acetate of Lime (gray)	C.	2 50	@	2 60
Alum (lump)	C.	1 75	@	2 00
Aluminum Sulfate	C.	1 40	@	1 75
Ammonium Carbonate, domestic	Lb.	8	@	8 1/2
Ammonium Chloride, gray	Lb.	6 1/4	@	6 1/2
Aqua Ammonia (drums) 16°	Lb.	2 1/4	@	2 1/2
Arsenic, white	Lb.	4	@	4 1/2
Barium Chloride	C.	1 70	@	1 80
Barium Nitrate	Lb.	5 1/4	@	5 1/2
Barytes (prime white, foreign)	Ton	18 50	@	22 50
Bleaching Powder (35 per cent)	C.	1 35	@	1 1/2
Blue Vitriol (bulk)	Lb.	5 1/4	@	5 1/2
Borax, crystals (bags)	Lb.	3 3/4	@	4 1/4
Boric Acid, crystals (powd.)	Lb.	7	@	7 1/2
Brimstone (crude, domestic)	Ton	22 00	@	22 50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	85	@	1 10
Chalk (light precipitated)	Lb.	4	@	5
China Clay (imported)	Ton	11 50	@	18 00
Feldspar	Ton	7 00	@	9 00
Fuller's Earth, powdered, Foreign	Ton	14 50	@	15 00
Green Vitriol (bulk)	C.	55	@	60
Hydrochloric Acid (18°)	C.	1 15	@	1 55
Iodine (resublimed)	Lb.	3 05	@	3 10
Lead Nitrate	Lb.	8 1/8	@	8 1/4
Lithium Carbonate	Lb.	65	@	70
Litharge (American)	Lb.	6 1/2	@	7
Magnesia (powdered)	Lb.	5 1/2	@	6
Magnesite (raw)	Ton	30 00	@	31 00
Nitric Acid, 36°	Lb.	37 3/8	@	4 1/2
Phosphoric Acid (sp. gr. 1.75)	Lb.	21 1/2	@	25 1/2
Phosphorus	Lb.	35	@	90
Plaster of Paris	Bbl.	1 50	@	1 70
Potassium Bichromate, 50°	Lb.	6 3/4	@	7
Potassium Bromide	Lb.	39	@	40
Potassium Carbonate (calcined) 80 @ 85%	C.	3 40	@	3 65
Potassium Chlorate, crystals	Lb.	9	@	10 1/2
Potassium Cyanide (bulk) 98-99%	Lb.	19	@	24
Potassium Hydroxide	C.	3 75	@	4 75
Potassium Iodide (bulk)	Lb.	2 60	@	2 65
Potassium Nitrate (crude)	Lb.	5	@	—
Potassium Permanganate (bulk)	Lb.	9 3/4	@	11
Quicksilver, Flask	Lb.	39 00	@	40 00
Red Lead (American)	Lb.	6 1/2	@	7
Salt Cake (glass-makers')	C.	55	@	65

Silver Nitrate	Oz	38 1/2	@	41
Soapstone in bags	Ton	10 00	@	12 00
Soda Ash (28 per cent)	C.	70	@	80
Sodium Acetate	Lb.	4	@	4 1/2
Sodium Bicarbonate (English)	Lb.	2 1/4	@	3
Sodium Bicarbonate (domestic)	Lb.	1	@	1 1/2
Sodium Bichromate	Lb.	4 1/2	@	5
Sodium Carbonate (dry)	Lb.	60	@	80
Sodium Chlorate	Lb.	8 1/4	@	9 1/2
Sodium Hydroxide, 60 per cent	C.	1 60	@	1 65
Sodium Hyposulfite	C.	1 30	@	1 60
Sodium Nitrate, 95 per cent, spot	C.	2 62 1/2	@	—
Sodium Silicate (liquid)	C.	65	@	1 50
Strontium Nitrate	Lb.	6 1/2	@	7 1/2
Sulfur, Flowers (sublimed)	C.	2 20	@	2 60
Sulfur, Roll	C.	1 85	@	2 15
Sulfuric Acid, 60° B.	C.	85	@	1 00
Talc (American)	Ton	15 00	@	20 00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	14 1/4	@	14 1/2
Tin Oxide	Lb.	50	@	52
White Lead (American, dry)	Lb.	5 1/4	@	6
Zinc Carbonate	Lb.	8	@	8 1/2
Zinc Chloride (granulated)	Lb.	4 1/2	@	5
Zinc Oxide (American process)	Lb.	5 3/8	@	6 3/8
Zinc Sulfate	Lb.	2 1/2	@	2 3/4

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	42	@	45
Black Mineral Oil, 29 gravity	Gal.	13 1/2	@	14
Castor Oil (No. 3)	Lb.	87 1/8	@	10
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	5 80	@	5 85
Cottonseed Oil (crude), f. o. b. mill	Gal.	43	@	44
Cottonseed Oil (p. s. y.)	Lb.	—	@	7
Cylinder Oil (light, filtered)	Gal.	21 1/2	@	32
Japan Wax	Lb.	9 1/4	@	10
Lard Oil (prime winter)	Gal.	95	@	1 00
Linseed Oil (double-boiled)	Gal.	46	@	48
Menhaden Oil (crude)	Gal.	26	@	28
Neatsfoot Oil (20°)	Gal.	98	@	1 10
Paraffine (crude, 120 & 122 m. p.)	Lb.	3 1/2	@	3 1/4
Paraffine Oil (high viscosity)	Gal.	26	@	28
Rosin ("F" grade)	Bbl.	5 75	@	5 85
Rosin Oil (first run)	Gal.	34	@	38
Shellac (tn)	Lb.	19	@	19 1/2
Spermaceti (cake)	Lb.	30	@	35
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Spindle Oil, No. 200	Gal.	18	@	19
Stearic Acid (double-pressed)	Lb.	9 1/4	@	9 3/4
Tallow (acidless)	Gal.	64	@	67
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	43	@	44

METALS

Aluminum (No. 1 ingots)	Lb.	26 3/4	@	28
Antimony (Hallet's)	Lb.	8 1/2	@	9
Bismuth (New York)	Lb.	2 10	@	2 15
Bronze powder	Lb.	50	@	3 00
Copper (electrolytic)	Lb.	15 60	@	15 1/4
Copper (lake)	Lb.	15 5/8	@	15 1/2
Lead, N. Y.	Lb.	4 35	@	4 40
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	46 00	@	—
Silver	Oz.	59 3/8	@	60
Tin	Lb.	50 1/8	@	51
Zinc	Lb.	5 65	@	6

FERTILIZER MATERIALS

Ammonium Sulfate	C.	3 15	@	—
Blood, dried	Unit	2 95	@	—
Bone, 4 1/2 and 50, ground, raw	Ton	28 50	@	—
Calcium Nitrate (Norwegian)	C.	2 40	@	—
Castor meal	Unit	nominal		
Fish Scrap, domestic, dried	Unit	nominal		
Mowrah meal	Ton	9 00	@	—
Phosphate, acid, 16 per cent bulk	Ton	7 50	@	8 00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	3 00	@	3 25
Tennessee, 70-80 per cent	Ton	5 00	@	5 50
Potassium, "muriate," basis 80 per cent	Ton	38 55	@	—
Pyrites, furnace size, imported	Unit	0 13 1/2	@	—
Tankage, high-grade	Unit	2 90	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

JUNE, 1913

No. 6

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, J. M. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblentz, W. C. Geer, F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhenny, Wm. McMurtrie, M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly. Foreign postage, seventy-five cents. Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

No claims will be allowed unless made within 60 days

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:		The Governments' Interests in the Pulp and Paper Industry. By Martin L. Griffin.....	500
The Corrosion of Iron and Steel...	444	The Training of the Fermentologist. By Carl A. Nowak.....	502
Efficiency Studies in the Hardwood Distillation Industry	445	WILLARD GIBBS MEDAL AWARD:	503
ORIGINAL PAPERS:		Chairman's Address. By Julius Stieglitz.....	504
Copper in Steel—The Influence on Corrosion. By D. M. Buck.....	447	Presentation Address. By W. D. Richardson.....	505
Intergranular Cement in Metals. By W. E. Ruder.....	452	Address of Acceptance: The Chemical Constitution of Resinous Phenolic Condensation Products. By L. H. Backeland.....	506
Influence of Various Elements on the Corrodibility of Iron. By Charles F. Burgess and James Aston.....	458	CURRENT INDUSTRIAL NEWS:	
Characteristics and Differentiation of Native Bitumens and their Residuals. By Clifford Richardson.....	462	The Electrochemical Industries of Italy.....	511
Distillation of Tar. By P. P. Sharples.....	466	The Match Industry of Sweden.....	511
The Determination of Sulfate in Ammonium Sulfate Solution with Special Reference to the Testing of Illuminating Gas. By R. S. McBride and E. R. Weaver.....	469	The Recovery of Brass from Foundry Cinders.....	512
The Determination of Sulfur in Illuminating Gas. By R. S. McBride and E. R. Weaver.....	474	An Electrolytic Theory of the Corrosion of Iron.....	512
Some Results of the Hypochlorite Disinfection of the Baltimore City Water Supply. By J. Bosley Thomas and Edgar A. Sandman.....	476	The Use of Cast Iron Briquettes in German Foundries.....	513
Wild Lettuce Rubber. By Charles P. Fox.....	477	The Bisulfite Process for the Extraction of Zinc.....	513
A Comparative Study of the Composition of Hops Grown in Different Parts of the World. By H. V. Tartar and B. Pilkington.....	478	The Toxicity of Lead Paints.....	513
A Critical Study of the Factors Causing the Modified Babcock to Run Lower on Ice Cream than the Roese-Gottlieb Method. By J. O. Halverson.....	480	The Potash Situation in Austria.....	513
Tincture of Iodine. By L. F. Kebler.....	484	Waste Sulfite Liquor as a Fertilizer.....	513
The Application of Folin's Method for the Determination of Ammonia to Fertilizers. By Otto Folin and A. W. Bosworth.....	485	The Disposal of the Discharges from Packing-Houses.....	514
LABORATORY AND PLANT:		Substitutes for Gasoline.....	514
The Use of Natural Gas in Steam Boilers. By George W. Barnes.....	486	Artificial Leather from "Syrolit".....	514
A Vitriol Clay Combustion Tube with Tapered Outlet for the Determination of Carbon in Steels, Ferro Alloys and Graphite. By Charles Morris Johnson.....	488	Rubber in Hawaii.....	515
An Electric Desiccator for the Analysis of India Rubber and other Organic Compounds. By L. J. D. Healy.....	489	The use of "Humin" in the Purification of Sugar Factory Waste Waters.....	515
A Compact, Accurate Burette for Use in Nitrogen Work or Whenever Many Measurements of Standard are Necessary. By Frank C. Gephart.....	490	"Cellophane".....	515
A Combination Apparatus Stand. By E. R. Squibb & Sons.....	490	Safety Fuses and Detonators.....	515
MISCELLANEOUS:		Estimating on the Cost of Power Plants.....	515
Production and Industrial Application of By-product Coke Oven Gases. By J. Becker and L. B. Robertson.....	491	"The Hydro-Cator".....	516
Synthesis of Precious Stones. By I. H. Levin.....	495	The Rideal-Evans Chlorometer.....	516
		The Efficiency of Condenser Air Pumps.....	516
		A New Gas Scrubber.....	517
		SCIENTIFIC SOCIETIES:	
		Preliminary Report for the Committee on Coal Analysis of the American Society for Testing Materials and the American Chemical Society. By W. A. Noyes.....	517
		The Iron and Steel Institute Fellowship.....	528
		American Chemical Society—September Meeting.....	528
		American Institute of Chemical Engineers.....	528
		Bureau of Standards' Analyzed Samples.....	528
		Another Platinum Thief.....	528
		BOOK REVIEWS:	
		Chemical Industries of Belgium, Netherlands, Norway, and Sweden; The Principles of Applied Electrochemistry.....	528
		NEW PUBLICATIONS	529
		RECENT INVENTIONS	531
		MARKET REPORT	532

EDITORIALS

THE CORROSION OF IRON AND STEEL

It is now six years since the electrolytic theory in its developed form was offered as a basis for the explanation of the corrosion of iron and steel, and it seems worth while at this time to inquire regarding the accuracy of some of the conclusions to which it has led, as viewed in the light of present experience.

In the first place we have found that the factors controlling the rapidity or extent of corrosion are by no means so simple as they were at first thought to be. Many conditions which were considered of little or no importance have been found to exert a profound influence upon the reactions involved. For example, samples of iron and steel that exhibit marked differences in corrosion exposed in the normal condition in which they come from the mill, fail to show any difference upon exposure when they are first planed to a uniform surface. Apparently the mechanical strain to which the samples are subjected in the planer, masks or neutralizes the difference in corrosion inherent in the normal material. It is not surprising, therefore, that many conflicting results have been obtained and published from the investigators now interested in this work. Only those tests which have been carried on under identical conditions of surface finish, temperature, access of oxygen and moisture, general atmospheric conditions, etc., should be given any weight, and even when the greatest care is taken, generalizations must be drawn with caution.

One of the conclusions reached by a consideration of the electrolytic theory of corrosion which has proven misleading, is that homogeneity in material insures protection, while heterogeneity leads to rapid attack. While this is a corollary which may be logically drawn from the electrolytic theory and is doubtless in itself true, there are evidently other factors which superimpose themselves upon those due to differences in structure, producing a final effect contrary to that predicted. The iron of the old chain bridge at Newburyport, Mass., has withstood corrosion in a truly remarkable manner for the last ninety-eight years; and yet it is conspicuous for its heterogeneous structure. Large areas of perfectly pure iron, free from both carbon and slag, are mixed up with areas showing at least two kinds of slag and very high carbon; yet all withstand atmospheric corrosion. On the other hand, Burgess has shown that iron free from all contaminating elements which could segregate or produce a lack of uniformity, does not withstand rusting so well as the same iron to which has been added a little manganese, or copper, or nickel. This behavior is observed also in the case of the so-called pure irons made in an open-hearth furnace, and which are relatively free from carbon, manganese, sulfur, and other constituents prone to segregation, which have come to the writer's notice. While theoretically a very pure iron should withstand rust, there are apparently some factors present which more than offset any advantage

inherent in purity. Obviously conditions affecting the surface of the material so soon as rusting has started are important causes which have largely been overlooked and which demand more thorough investigation.

The most important advance in this field made in recent years is a knowledge of the effect of the addition of small amounts of copper to normal open hearth or bessemer steel. This result is most strikingly brought out on the paper of D. M. Buck, published in full on page 447 of *THIS JOURNAL*. The writer has, within a week, inspected with much interest the test roofs here described and can testify to the remarkable effect shown. While panels of bessemer and open hearth steel containing the ordinary amounts of metalloids have entirely failed, the corresponding panels made from these same heats of steel but to which a small amount of copper was added, are in a remarkable state of preservation. A panel of the so-called pure iron very low in metalloids, but containing one-half the amount of copper carried by the less pure steels is less attacked than those steels containing no copper, but is much less resistant than are those to which two-tenths of one per cent copper was added. Had copper been omitted entirely from this iron it would doubtless have succumbed even earlier. While these tests do not show that any steel however poorly made will, with the addition of copper, withstand atmospheric corrosion, they prove that it is copper, and not the absence of manganese and the other "impurities" which is the controlling factor. Several hypotheses have suggested themselves as explaining this marked effect of copper in causing steel to resist atmospheric corrosion, but as yet none are sufficiently tangible to afford a working theory.

Rapid progress has been made in acquiring that knowledge of the relation of pigments and finished paints to corrosion which is necessary to a better protection of iron and steel. Predictions founded on theory that a basic paint, or one containing a chromate pigment, would inhibit rusting, while one made up from lampblack or graphite would accelerate rusting, have, in the main, been found correct. The effect of the pigment upon the character of the oil film making up the paint, however, has shown itself also to be very important. Many basic pigments such as basic lead carbonate or zinc oxide which in themselves inhibit, do not withstand the weather; lampblack and graphite, on the other hand, make a very impervious and highly resistant paint film. The logical conclusion in protecting iron is, therefore, to use a basic priming coat, a second coat of a mixture of a basic pigment and a little lampblack, and when well dried out to apply a lampblack or graphite finishing coat. Experience has shown also the importance of brushing the paint well onto the iron; a good paint may fail on account of poor application.

Careful tests with galvanized work show that an

even coating of zinc is the all-important factor. The common practice of clean wiping galvanized ware is fatal to durability, since the protecting layer is not metallic zinc, but a thin deposit of a zinc-iron alloy. While, therefore, much has been accomplished in the way of making a more resistant base, there is still the necessity of a uniform substantial coating of spelter over the surface.

WM. H. WALKER.¹

EFFICIENCY STUDIES IN THE HARDWOOD DISTILLATION INDUSTRY

We hear a great deal about efficiency engineers and efficiency studies in business or in the mechanical side of various industries and about the great savings which have been obtained by the introduction of some new system of accounting or of some new method of handling a brick or a piece of iron. We have not heard so much about efficiency studies in purely chemical processes, probably because their application is not so direct and because they have been called by other names, such as "increasing the yield" or "improving the products." But they are just as important and just as effective in chemical as in mechanical processes, although they are usually more complicated in the former, since a change in one part of a chemical process is likely to have an effect in several other parts of the process.

The hardwood distillation industry has some particularly interesting problems which might be made the subjects of efficiency studies, and a few of these will be briefly outlined. Some are well recognized problems and are given only as examples of the application of efficiency studies, while others are not so generally recognized as important.

Variation in Yields from Different Raw Materials.—The question of the variation in yields due to the kind of raw material distilled has never had proper consideration. In this country the usual raw material consists of mixtures of different species of hardwoods in various unknown proportions, depending upon the natural occurrence of these species in the forests from which the wood supply is obtained; beech, birch and maple predominate, but there are also small amounts of elm, ash, oak, ironwood, etc. Some recent work of the Forest Service² has indicated the possible variation in yields due to species and has shown the importance of considering this factor in judging the value of a raw material. Of course in a plant already established this question would probably not be of importance because it is likely to have only one certain mixture of species available and it is doubtful whether sorting of the species would be practicable. But in establishing new plants a consideration of the species available and their relative costs is very important. For instance, the question might arise,

"Which is the most favorable source of raw material, tupelo at \$2 per cord or birch at \$2.50?" The solution of this question would depend almost entirely upon the value of the products per cord from the two classes of material, since the cost of distilling the wood and refining the products would differ only slightly. It would therefore be necessary only to determine the yields per cord from each of the two species and find whether the difference in the value of the products made up for the difference in cost.

However, in comparing two species which differ considerably in weight per cord, it would be necessary to consider also the difference in cost of distilling the wood and refining the distillate. For instance, in comparing oak (weight per cord with 15 per cent moisture about 4300 lbs.) with red gum (weight per cord with 15 per cent moisture about 3300 lbs.) it can be seen that more heat would be required to distil a cord of the former and, assuming the same percentage of pyroligneous acid, 40 per cent, in both cases, there would be 400 lbs. more pyroligneous acid per cord to refine in the case of the oak. In distilling the wood the extra fuel would be the only added expense, but in refining the distillate there would be required an increase in capacity of the refining apparatus as well as extra fuel. In comparing the values of two species which differ in weight it is therefore necessary to take into account other things beside just the yield of products and the cost per cord.

A very similar study is the determination of the relative values of different forms of material from the same species. This question has never been completely solved, and various opinions have been held concerning the relative values of different forms. It has lately been shown³ that there may be considerable variation in the yields from different parts of the same tree and in some species the slabs, which, on account of the bark, are usually considered inferior, have given higher yields of both alcohol and acetic acid than the heartwood without bark. This difference in yields from different forms is not the same in all species and therefore a separate study is required for each species.

A more complicated study is the determination of the minimum size of material which can be economically used, since there are several effects of variation in size which must be combined into the final results.

Let us consider a case where a wood distillation plant is installed to use the mill and forest waste from a hardwood lumbering operation; what shall be the limit in size of limbs and slabs to be distilled? There are four effects of size which must be taken into account in this problem: (1) The effect of size on composition of material and therefore on yields is very important. A small slab naturally means a slab with a large proportion of bark and in the same way the size of a limb affects the proportion of bark and sapwood; therefore, the yields of the products from different sizes of slabs and limbs must be determined. (2) The cost of collection and handling the material also varies with the size of the piece; it is very evident

¹ Abstract of paper presented before the New York Section of the Society of Chemical Industry, Chemists' Club, April 25, 1913.

² "Yields Obtained by the Destructive Distillation of Different Forms and Species of Hardwood," L. F. Hawley and R. C. Palmer, Eighth Int. Congr. App. Chem., Vol. 6, p. 138, and THIS JOURNAL, 4, 789. This work has been extended to include another species and check determinations on several of the previous species; it will be published in more complete form as a Forest Service Bulletin.

³ Hawley and Palmer, *Loc. cit.*

that the time required for piling a cord of wood containing, say, 150 sticks, would be much less than with a cord containing 450 sticks. (3) Smaller sized material also decreases the capacity of the retorts. A car $4' \times 4' \times 8'$ still holds a "cord" but that "cord" contains less wood by weight when composed of small pieces; this is especially true in the case of small limbs which are apt to be irregular and hence to increase the size of the interstices between the sticks. (4) Between certain limits a decrease in the size of the pieces of wood undoubtedly makes the distillation easier, but below these limits the difficulty of distillation is increased very rapidly. It is very probable, however, that in the case of slabs and limbs this low limit would not be reached because the cost of handling would first have become prohibitive.

The combination of these four effects of size in the proper proportions in order to determine the relative values of raw materials of different sizes is seen to be a problem requiring considerable experimentation and calculation.

Moisture Content.—The drying of wood before distillation is a general practice in this country, usually being accomplished by piling in the open air for a certain length of time, but there is apparently no well ordered scheme of drying so as to derive the maximum benefit at the minimum cost. The first most obvious effect of the moisture content of the wood distilled is on the amount of heat required to distil the wood and to refine the products; the excess water must not only be distilled from the wood but redistilled once or twice more, depending on the refining methods, during the refining process. If the necessity for the distillation of the excess water were the only effect due to high moisture content, the computation of the extra expense would be comparatively easy, but there are other effects also. The increased moisture content may increase the length of time required for distillation and therefore reduce the capacity of the retorts; the extra water in the pyroligneous acid requires enlarged refining apparatus; and finally, according to Klar,¹ the yields of acetic acid are inversely proportional to the amount of water in the wood. In determining the optimum moisture content of the wood at any particular plant it would be necessary to balance the cost of drying against the gains due to saving of fuel, to increase of capacity of distilling and refining apparatus, and to increase of yields. This study would require a large amount of both experimentation and calculation.

Effect of Temperature on Yields.—The effect of the temperature of distillation on the yields has never been given sufficient practical consideration. It is generally understood that slow² distillation improves the yield of valuable products, but there does not

seem to be any definite conception of how much of an effect can be produced in this way. This lack of information is probably due to the fact that most forms of commercial apparatus are designed for distillation under certain definite conditions, and it is difficult to vary these conditions to any great extent. The tendency in American practice, true to the American industrial temperament, has also been toward rapidity and low labor cost in handling raw material, so that there has been neither opportunity nor tendency to investigate along this line.

It is very certain that the maximum possible yields are not nearly attained; the commercial yields of the acetate of lime are only about 65 per cent of what the wood is capable of furnishing.¹ Would it be advisable to attempt to obtain this increased yield? The extra expense which must be considered would consist of increased cost of distilling apparatus per cord of wood and probably increased cost of handling the wood and the charcoal. The fuel for distilling and the cost of refining would be affected very little. The cost of the wood has become such a large item in the expenses of wood distillation and the value of the acetate of lime has increased so much that the time may have arrived to attempt to increase the yields per cord of wood rather than to increase the capacity of the plant in cords per day.

Heat Economy in Refining.—The usual refining process consists of a series of distillations with complete condensation of the distillates in water-cooled condensers. These distillations and condensations often require amounts of heat and cooling water respectively sufficient for the distillation and condensation of about $2\frac{1}{2}$ times the total crude distillate. There are therefore many chances for combinations of these different distillations² in such a way that the vapors from one serve to furnish the heat for another and thus the steam and water required may be cut down considerably. Along this line the efficiency studies would be for the purpose of determining whether the heat saved by a certain combination of steps would be sufficient justification for the extra cost of apparatus or for determining which of several possible changes in refining procedure was the most promising. The cost of fuel is the big deciding factor in such cases.

Products Unrecovered from the Tar.—The tar, both from the settling tanks and from the crude pyroligneous acid still, retains in solution both methyl alcohol and acetic acid; these cannot be recovered by distillation of the tar with the dry heat applicable by means of ordinary pressure steam, and the usual custom is to heat the tar with closed steam coils and then blow in a jet of steam. Since the acetic acid has a boiling point above that of water the proportion of acid in the distillate is small and decreases slowly; how far is it economical to carry this distillation? There are several factors to be balanced in this case. In favor of continuing the distillation we have only the value

¹ "Technologie der Holzverkohlung," p. 77. This report does not give the exact relation between the moisture content and the yields so that this would have to be determined. This effect of moisture content would probably also vary with different methods of distillation.

² In the same distilling vessel, slow distillation is the same as low temperature distillation, because the only way to slow down is to decrease the temperature; therefore the "effect of temperature" is similar to the "effect of speed." Of course by decreasing the size of the vessel, the speed of distillation may be increased without increasing the temperature.

¹ Hawley and Palmer, *Loc. cit.*

² A very complete discussion of the heat economy obtained by several different combinations of this kind can be found in Klar's "Technologie der Holzverkohlung," Chap. 15.

of the acid removed; in favor of stopping we have the cost of continuing and the cost of refining the distillate. Both of these costs include not only the steam required but the capacity of the apparatus as well, so that a rather complex computation is required to settle the point.

Products Lost in the Gas.—The non-condensable gas which escapes from the retort condensers carries with it a certain proportion of vapor of pyrolygneous acid. The proportion of this vapor in the gas depends only on the temperature to which the products are cooled in the condenser, but even with the best cooling there will still be some vapor lost. As far as the writer knows, this loss of pyrolygneous acid is not being prevented at any plant in this country, although in Europe the use of gas scrubbers for this purpose is quite common.¹

In determining the advisability of installing scrubbers to recover at least part of the valuable products from the gas, the cost of collecting and washing the gas and of refining the wash water must be balanced

against the value of the alcohol and acetic acid saved. The cost of washing the gas and of refining the wash water and the amount of products recovered will vary considerably, depending on the conditions. For instance, if with the same amount of wash water a longer scrubber is used, a larger proportion of products will be saved; or if in the same scrubber more wash water is used, a larger proportion of products will also be saved, but at the same time the wash water will be more dilute and therefore the costs of refining will be greater. It is therefore necessary to have just the proper relation between these variable factors in order to obtain the best results.

It is hoped that these few examples of efficiency studies will indicate some of the opportunities for increasing the efficiency of hardwood distillation operations by means of technical investigations.

L. F. HAWLEY.

LABORATORY
ARTHUR D. LITTLE, INC.
BOSTON

ORIGINAL PAPERS

COPPER IN STEEL—THE INFLUENCE ON CORROSION²

By D. M. BUCK

In order to establish the value of small amounts of copper in steel when exposed to natural corrosion and under atmospheric conditions, a series of tests was undertaken by the writer, and in order that a thorough understanding may be had of the results of these tests, we believe it will not be out of place to briefly describe the preparation of the steels entering into this investigation.

In order to avoid the possible uncertainty in comparing different heats of steel with and without copper, and in order that the conditions, except the copper content, should be identical, it was decided for these comparisons to copperize portions of heats, leaving other portions of the same heats in their original conditions.

Three heats were used: One a regular Basic Open Hearth of the following analysis:

C, 0.10; Mn, 0.34; S, 0.034; P, 0.019.

A second Basic Open Hearth heat was rephosphorized, giving this analysis:

C, 0.13; Mn, 0.45; S, 0.036; P, 0.042.

The third heat was regular Bessemer steel of the following analysis:

C, 0.08; Mn, 0.46; S, 0.070; P, 0.096.

In pouring the Open Hearth heats several ingots were first poured without the introduction of copper, then to four ingots sufficient copper was added to obtain in two of them about 0.15 per cent and the other two about 0.25 per cent copper in the finished product. The Bessemer heat was treated in exactly the same way, except that, since the average Bessemer heat is too small to furnish six ingots of the size de-

sired, only two ingots were copperized, aiming at the same contents as in the case of the Open Hearth. The copper was added to the molds a little at a time as they were filling, and that the resultant steel was uniform in its copper content was demonstrated by many analyses of the bars and of the finished sheets. Indeed, that copper easily diffuses through the bath of molten steel, and does not segregate on cooling, is a well established fact.

Six ingots were then taken from each of the Open Hearth heats, two normal, two with 0.15 copper and two with 0.25 copper, and three ingots from the Bessemer heat, one normal, and one with each content of copper.

The fifteen ingots thus prepared were carried through the usual mill operations, each bar as cut and each sheet as rolled being chalk marked so that no confusion could possibly occur, and in the end one of each lot was again carefully analyzed as a double check on the operations.

One ingot of each grade of Open Hearth was rolled into 16-gauge and the other into 27-gauge sheets, 30 inches \times 96 inches, while in the case of the Bessemer steel, one-half of each ingot was rolled into 16- and the other half into 27-gauge. All grades were subjected to exactly the same treatment, being rolled by the same crews, and annealed in the same furnaces at the same time, and the finish was such as to conform with that of the competitive sheets used in this test. From 24 to 36 sheets of each of the 9 grades, both gauges, making 18 lots in all, were then sheared to 24 inches \times 96 inches, thus obtaining a strip 6 inches wide from each sheet. These strips were sheared into 2 \times 4 inch test pieces, stenciled with distinguishing marks, and were used for corrosion tests which will be described later. The 24 \times 96 inch sheets were corrugated in the usual way, and

¹ Klar: "Technologie der Holzverkohlung," p. 161.

² Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913.

eight to twelve sheets of each grade shipped to each of three testing stations. One of these is located in the Pennsylvania Coke Regions, where the air contains notable amounts of sulfurous and sulfuric acids and other fumes from the coke ovens. In this district iron and steel, unless protected, corrode very fast. Another station is located on the Sea Coast, where the air carries sodium chloride. The third is in a rural community, where the air is quite pure and free from added corrosive agents.

At each of these locations a skeleton wooden building was erected, 40 feet \times 80 feet, with a sloping roof at an angle of about 18° , with the low side about 6 feet from the ground. The buildings were entirely open and free to the passage of air on all four sides, and the roofs were uncovered until the sheets were

November, 1911, and were entirely unprotected by paint or other coating from the first (except the thin film of oxide always present on an annealed sheet), allowing natural corrosion to start immediately and to proceed without interruption. The 16-gauge sheets were placed on one-half of the roof, and the 27-gauge on the other half.

The sheets at all of the test stations were inspected from time to time by the writer, and by other independent inspectors, and within a short time after corrosion had started the higher copper steels were showing a considerable advantage over the others.

Panels 1, 4 and 7 (see Fig. I), which contain no copper, were rough to the touch and an examination of the surface of the steel under the rust gave evidence of well developed pitting. Panel 10, the low carbon

16 Gauge.			27 Gauge.		
Nº7 Composition. C. Mn. S. P. Cu. .08 .46 .070 .098 Trace	Nº9 Composition. C. Mn. S. P. Cu. .07 .46 .069 .095 .327		Nº7 Composition. C. Mn. S. P. Cu. .05 .45 .076 .100 Trace.	Nº9 Composition. C. Mn. S. P. Cu. .05 .44 .075 .099 .340	
Nº8 Composition. C. Mn. S. P. Cu. .08 .45 .070 .094 .267	Nº10 Composition. C. Mn. S. P. Cu. .03 .03 .034 .003 .061		Nº8 Composition. C. Mn. S. P. Cu. .05 .44 .082 .101 .226	Nº10 Composition. C. Mn. S. P. Cu. .02 .03 .036 .003 .069	
Nº1 Composition. C. Mn. S. P. Cu. .10 .34 .034 .019 Tr.	Nº2 Composition. C. Mn. S. P. Cu. .10 .34 .035 .028 Tr.	Nº3 Composition. C. Mn. S. P. Cu. .10 .35 .033 .019 .220	Nº1 Composition. C. Mn. S. P. Cu. .06 .35 .033 .018 Tr.	Nº2 Composition. C. Mn. S. P. Cu. .06 .35 .035 .016 Tr.	Nº3 Composition. C. Mn. S. P. Cu. .06 .33 .035 .018 .250
Nº4 Composition. C. Mn. S. P. Cu. .13 .48 .035 .042 Tr.	Nº5 Composition. C. Mn. S. P. Cu. .13 .44 .035 .042 Tr.	Nº6 Composition. C. Mn. S. P. Cu. .14 .46 .038 .043 .265	Nº4 Composition. C. Mn. S. P. Cu. .09 .47 .037 .043 Tr.	Nº5 Composition. C. Mn. S. P. Cu. .10 .46 .035 .043 .176	Nº6 Composition. C. Mn. S. P. Cu. .07 .47 .038 .043 .284

FIG. I—DIAGRAM OF TEST ROOFS ERECTED IN 1911, BY AMERICAN SHEET AND TIN PLATE COMPANY

put on, the purlins being 92 inches apart, thus allowing for a 2 inch hold on each end of the sheets. The sheets were arranged in panels, each grade being separated from the other by an open space. Open spaces were left between each course, so that the drip from one row did not run onto the row below.

In addition to the nine grades before mentioned, there were purchased on the open market, 27-gauge and 16-gauge sheets of the following average analysis: C, 0.02; Mn, 0.03; S, 0.034; P, 0.003; Cu, 0.06–0.07.

These sheets were exposed at each of the test stations at the same time as the others and under identical conditions.

All of the sheets were placed on the roofs during

and manganese material with only 0.07 copper, was not quite so rough, and the pitting not quite so well developed, while panels 2, 3, 5, 6, 8 and 9, which contain 0.15 to 0.34 copper, were fairly smooth to the touch with scarcely any pitting. An interesting fact was noted regarding the color of the rust on the various panels. The oxide on the non-copper steels was a bright red and loosely adherent. That on panel 10 was a little darker, while the copper-bearing steels carried a dark brown, closely adhering oxide. It was possible to distinguish them by their color at a considerable distance from the building.

Fig. II is a photograph of the 27-gauge side of the roof in the coke regions, taken June 27, 1912. The

non-copper panels 1, 4 and 7 were failing and falling off, having rusted entirely through. All of the copper-bearing steels were still in excellent condition.

Fig. III is a photo of the same roof taken Dec. 7,

as Fig. III. All of the copper-bearing panels are still intact, and will last several months before ultimate failure. This roof was again inspected early in March, 1913, and panel 10 had entirely disappeared, while



FIG. II



FIG. III

1912. Panels 1, 4 and 7 had entirely disappeared, and 10, the low carbon and manganese material, had failed to the extent of dropping off.

Fig. IV is a nearer view of panel 3 and Fig. V a nearer view of panel 10, both taken on the same day

all of the copper-bearing steel sheets were still in place.

Fig. VI is a similar photo of the 27-gauge side of the seashore roof, taken Sept. 7, 1912. The panels were in about the same condition as those in the coke regions were some months earlier. Unfortunately

a few weeks after these sheets were placed, an unusually severe gale ripped off all of panel 9 and parts of 7, 10, 3 and 6.

Fig. VII is a photo of the 27-gauge side of the roof located in a rural district, taken Feb. 20, 1913. While none of the copper-bearing materials have failed up to the present time at either of the last two roofs, yet panel 10, at both places, is in very poor condition and will fail very soon, much before the other copper-

pared and exposed after first removing all surface oxides. After a suitable time had elapsed, and certain of the test pieces had rusted entirely through, they were taken down and reweighed, after first removing all rust by a solution of ammonium citrate, which takes off the oxide without attacking the underlying iron.

Table I gives the results obtained on the 2×4 inch

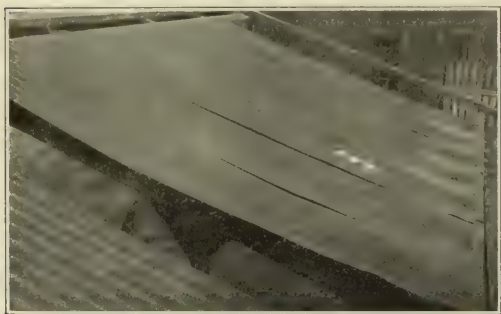


FIG. IV

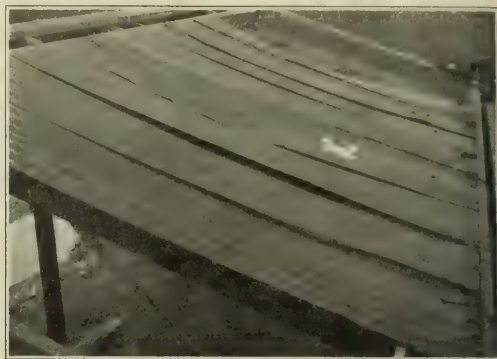


FIG. V

bearing steels, thus checking up the results obtained in the coke regions. The 16-gauge sheets at all of the test stations are giving the same relative differences as the 27-gauge, but being four times as thick, are not yet in condition to reveal their differences in a large photograph.

At the same time that the large sheets were exposed, a series of 2×4 inch test pieces, cut from the

test pieces exposed in the coke regions, Table II those at the seashore, and Table III those in the rural district. The tables are arranged to show the relative values on the basis of 100 for greatest amount of corrosion at each station, and the others in their respective values. It will be noted that in every case the steels with copper additions have shown a marked resistance to corrosion as compared with the non-copper



FIG. VI

same sheets, were carefully weighed on a chemical balance, then mounted in wooden racks, with free access to the weather, and exposed at each station. Six pieces of each grade, each piece from a different sheet, were used in this test and a duplicate set pre-

steels, having on the average nearly twice the life. There appears to be very little difference between the grades containing 0.15 copper and those with 0.24 to 0.34, while the material with low carbon and manganese and with 0.06 to 0.07 copper take an inter-

mediate position between the copper-bearing steels and those without copper. It will be noted that the results on the weighed test pieces check up very closely the results on the full-sized sheets.

Accelerated acid tests were also made on 2 X 4 inch test pieces, from the same sheets as were used in the corrosion tests, and Table IV gives the results

amount of copper present. In this regard the acid tests differ from the actual weather tests. The copper-bearing steels resist the atmosphere from 1½ to 2 times as well as the normal steels without copper, and there is little or no difference in the average between a copper content of 0.15 and 0.30.

The writer has never tested a normal non-copper-



FIG. VII

of these tests. The copper-bearing Open Hearth and Bessemer steels resist the acid from 50 to 100 times as well as the non-copper steels, and within the limits of the copper content of the steels used in this test, the resistance to the acid is directly proportional to the

bearing steel or iron which has any marked resistance to the action of sulfuric acid, neither has he found a single instance where steel carrying between 0.15 and 1.00 per cent of copper did not show a very marked resistance to the same acid, and, indeed, the presence or absence of copper is strongly indicated by the

TABLE I—SHOWING RELATIVE LOSSES ON 2 X 4 INCH TEST PIECES

Exposed in coke regions November 21, 1911, and taken down August 14, 1912
(Each result is the average of six pieces)

GRADE	PANEL	GA.	ANALYSIS (PERCENTAGES)					RELATIVE LOSSES 100 =	
			C	Mn	S	P	— POSI- TION CORROSION	GREATEST	
Bessemer..	8	27	0.05	0.44	0.082	0.101	0.23	1	39.09
Bessemer..	9	27	0.05	0.44	0.075	0.099	0.34	2	39.61
Bessemer..	9	16	0.07	0.46	0.069	0.095	0.33	3	41.57
Open Hearth	5	27	0.10	0.46	0.035	0.043	0.17	4	42.09
Open Hearth	6	27	0.07	0.47	0.038	0.043	0.25	5	42.22
Open Hearth	3	27	0.06	0.33	0.035	0.018	0.25	6	43.27
Open Hearth	2	27	0.06	0.35	0.036	0.018	0.16	7	43.92
Bessemer..	8	16	0.08	0.45	0.070	0.094	0.21	8	44.05
Open Hearth	6	16	0.14	0.46	0.038	0.043	0.27	9	46.67
Open Hearth	5	16	0.13	0.44	0.035	0.012	0.18	10	46.67
Open Hearth	3	16	0.10	0.35	0.033	0.019	0.23	11	47.32
Open Hearth	2	16	0.10	0.34	0.035	0.020	0.16	12	48.36
Low C and low Mn material	10	27	0.02	0.03	0.036	0.003	0.07	13	50.19
Low C and low Mn material	10	16	0.03	0.03	0.034	0.003	0.06	14	53.20
Open Hearth	4	16	0.13	0.45	0.035	0.042	0.00	15	74.64
Open Hearth	4	27	0.09	0.47	0.037	0.043	0.00	16	78.16
Bessemer..	7	16	0.08	0.46	0.070	0.098	0.00	17	91.64
Bessemer..	7	27	0.05	0.45	0.076	0.100	0.00	18	96.86
Open Hearth	1	16	0.10	0.34	0.034	0.019	0.00	19	98.82
Open Hearth	1	27	0.06	0.35	0.033	0.018	0.00	20	100.00

TABLE II—SHOWING RELATIVE LOSSES ON 2 X 4 INCH TEST PIECES
Exposed at seashore November 28, 1911, and taken down September 7, 1912
(Each result is the average of six pieces)

GRADE	PANEL	GA.	ANALYSIS (PERCENTAGES)					RELATIVE LOSSES 100 =	
			C	Mn	S	P	— POSI- TION CORROSION	GREATEST	
Bessemer..	9	27	0.05	0.44	0.075	0.099	0.34	1	51.12
Bessemer..	8	27	0.05	0.44	0.082	0.101	0.23	2	51.12
Open Hearth	6	27	0.07	0.47	0.038	0.043	0.25	3	51.96
Open Hearth	5	27	0.10	0.46	0.035	0.043	0.17	4	55.03
Open Hearth	3	27	0.06	0.33	0.035	0.018	0.25	5	55.59
Bessemer..	8	16	0.08	0.45	0.070	0.094	0.21	6	56.42
Bessemer..	9	16	0.07	0.46	0.069	0.095	0.33	7	56.70
Open Hearth	3	16	0.10	0.35	0.033	0.019	0.23	8	57.54
Open Hearth	5	16	0.13	0.44	0.035	0.042	0.18	9	58.94
Open Hearth	2	27	0.06	0.35	0.036	0.018	0.16	10	58.94
Open Hearth	6	16	0.14	0.46	0.038	0.043	0.27	11	60.90
Open Hearth	2	16	0.10	0.34	0.035	0.020	0.16	12	64.81
Low C and low Mn material	10	27	0.02	0.03	0.036	0.003	0.07	13	64.81
Low C and low Mn material	10	16	0.03	0.03	0.034	0.003	0.06	14	65.37
Open Hearth	4	27	0.09	0.47	0.037	0.043	0.00	15	65.60
Open Hearth	4	16	0.13	0.45	0.035	0.042	0.00	16	70.39
Open Hearth	1	27	0.06	0.35	0.033	0.018	0.00	17	87.99
Open Hearth	1	16	0.10	0.34	0.034	0.019	0.00	18	88.83
Bessemer.....	7	27	0.05	0.45	0.076	0.100	0.00	19	98.32
Bessemer..	7	16	0.08	0.46	0.070	0.098	0.00	20	100.00

TABLE III—SHOWING RELATIVE LOSSES ON 2 × 4 INCH TEST PIECES
Exposed in rural community December 3, 1911, and taken down November
16, 1912

(Each result is the average of six pieces)

GRADE	PANEL	GA.	ANALYSIS (PERCENTAGES)					RELATIVE LOSSES 100 =
			C	Mn	S	P	Cu	
Open Hearth..	2	27	0.06	0.35	0.036	0.018	0.16	1
Bessemer.....	9	27	0.05	0.44	0.075	0.099	0.34	2
Open Hearth..	2	16	0.10	0.34	0.035	0.020	0.16	3
Bessemer.....	8	27	0.05	0.44	0.082	0.101	0.23	4
Bessemer.....	9	16	0.07	0.46	0.069	0.095	0.33	5
Open Hearth..	3	27	0.06	0.33	0.035	0.018	0.25	6
Open Hearth..	5	27	0.10	0.46	0.035	0.043	0.17	7
Open Hearth..	5	16	0.13	0.44	0.038	0.042	0.18	8
Open Hearth..	6	27	0.07	0.47	0.038	0.043	0.25	9
Open Hearth..	3	16	0.10	0.35	0.033	0.019	0.23	10
Bessemer.....	8	16	0.08	0.45	0.070	0.094	0.21	11
Low C and low Mn material..	10	16	0.03	0.03	0.034	0.003	0.06	12
Open Hearth..	6	16	0.14	0.46	0.038	0.043	0.27	13
Low C and low Mn material..	10	27	0.02	0.03	0.036	0.003	0.07	14
Open Hearth..	4	16	0.13	0.45	0.035	0.042	0.00	15
Open Hearth..	4	27	0.09	0.47	0.037	0.043	0.00	16
Open Hearth..	1	16	0.10	0.34	0.034	0.019	0.00	17
Bessemer.....	7	16	0.08	0.46	0.070	0.098	0.00	18
Open Hearth..	1	27	0.06	0.35	0.033	0.018	0.00	19
Bessemer.....	7	27	0.05	0.45	0.076	0.100	0.00	20

solubility of the steel in sulfuric acid. Inasmuch as a copper content also increases the resistance to atmospheric corrosion, a certain relation is established between the accelerated acid test and natural corrosion when comparing copper-bearing with non-copper-bearing steels or irons. On the other hand, many instances have been noted and published where the results of acid tests have been directly opposite to results given by the same steels in service. We have

TABLE IV—COMPARATIVE TESTS SHOWING SOLUBILITY OF VARIOUS STEELS
IN 25 PER CENT SULFURIC ACID AT 35° CENTIGRADE

Results are the average of four determinations on four different sheets of each grade.

Grades 1, 2 and 3 from same heat. Grades 4, 5 and 6 from same heat.
Grades 7, 8 and 9 from same heat.

GRADE	GA.	SYMBOL	ANALYSIS (PERCENTAGES)					PERCENTAGE LOSS AT END OF STATED PERIODS	
			C	Mn	S	P	Cu	18 hrs.	36 hrs.
Open Hearth....	16	1	0.10	0.34	0.034	0.019	Trace	16.83	42.26
Open Hearth....	16	2	0.10	0.34	0.035	0.020	0.160	1.50	2.06
Open Hearth....	16	3	0.10	0.35	0.033	0.019	0.230	0.87	1.38
Open Hearth....	16	4	0.13	0.45	0.035	0.042	Trace	31.29	78.15
Open Hearth....	16	5	0.13	0.44	0.035	0.042	0.177	1.25	2.16
Open Hearth....	16	6	0.14	0.46	0.038	0.043	0.265	1.22	1.68
Bessemer.....	16	7	0.08	0.46	0.070	0.098	Trace	99.00	100.00
Bessemer.....	16	8	0.08	0.45	0.070	0.094	0.207	2.09	4.40
Bessemer.....	16	9	0.07	0.46	0.069	0.095	0.327	1.22	1.88
Low C and low Mn material...	16	10	0.03	0.03	0.034	0.003	0.061	1.35	2.64
Open Hearth....	27	1	0.06	0.35	0.033	0.018	Trace	41.92	100.00
Open Hearth....	27	2	0.06	0.35	0.036	0.018	0.160	1.28	2.04
Open Hearth....	27	3	0.06	0.33	0.035	0.018	0.250	0.90	1.54
Open Hearth....	27	4	0.09	0.47	0.037	0.043	Trace	88.23	100.00
Open Hearth....	27	5	0.10	0.46	0.035	0.043	0.170	2.02	4.33
Open Hearth....	27	6	0.07	0.47	0.038	0.043	0.250	1.29	2.06
Bessemer.....	27	7	0.05	0.45	0.076	0.100	Trace	100.00	...
Bessemer.....	27	8	0.05	0.44	0.082	0.101	0.226	1.19	2.40
Bessemer.....	27	9	0.05	0.44	0.075	0.099	0.340	0.95	1.69
Low C and low Mn material...	27	10	0.02	0.03	0.036	0.003	0.069	4.75	9.08

several instances of this in the tables given with this paper. Steel No. 4 dissolved about twice as fast in acid as steel No. 1 (both without copper), see Table IV,

yet it showed much greater resistance to the weather in each of the three characters of atmosphere. Steel No. 5 dissolved more than twice as fast as steel No. 2 (both copper-bearing), while at two of the test stations it gives a greater resistance to the weather. Several other inconsistencies could be pointed out, and it is the writer's opinion that the accelerated acid test used for the purpose of determining the values of steels or irons in their resistance to corrosion is untrustworthy and apt to be misleading and should be abolished, and should copper-bearing steels be desired, the presence or absence of that element determined by chemical analysis.

It is a well-known fact that copper is electronegative to iron, and when placed in contact with iron it will stimulate corrosion in the latter element. That the reverse is true when the copper is alloyed with the iron and in solid solution in the crystal grains, may be due to the alloy taking in a measure the non-corrosive properties of the copper. It has also occurred to the writer that the alloy of copper and iron is less electro-positive to the first film of rust formed than is non-copper steel, and the consequent decrease in difference of potential lessens the corrosion.

It has been suggested by Dr. W. H. Walker that the copper prevents the oxides of manganese and iron, which may be present, from coming out of solid solution as the melt cools, and hence, although the oxides are still present, they are held uniformly dissolved, and not segregated between the iron crystals, as is normally the case. Sufficient work has not been done to form any definite conclusions, and it is not the intention of this paper to discuss this phase of the subject at length, but rather to place before you results which seem to prove that a small copper content in steel (approximately 0.2 per cent) materially increases the life of steel sheets when subjected to atmospheric corrosion.

PITTSBURG, PA.

INTERGRANULAR CEMENT IN METALS¹

By W. E. RUDER

In the study of metals, the microscope has revealed the fact that all solid metals, even the softest, have a distinct crystalline structure and that this structure has a great influence upon their mechanical properties. This has perhaps been most closely studied in the case of iron and steel, and the general conclusion to be drawn is that for greatest mechanical strength a very fine-grained structure is desirable. Stead² has pointed out that brittleness may be of two kinds, intergranular and cleavage, and that the latter is the most prevalent. The expression grain and granular, herein, refers to the allotriomorphic crystals of metal in distinction to the perfect cubic crystallization of the interior.

It was, I believe, first pointed out by Rosenhain and Ewing,³ and later confirmed by Stead and others, that fracture, in most metals, under normal conditions never occurs along the boundaries of the grains but

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913.

² *Metallographist*, 1, 289 (1898); 2, 85.

³ *Proc. Roy. Soc.*, 65, 85 (1899).

always through the grains, *i. e.*, it is a cleavage fracture.

This greater strength of the boundaries is, then, of considerable importance, and the question of its composition naturally arises. Until quite recently, however, there has been very little investigation of these boundaries and their possible composition.¹ Rosenhain and Ewing first advanced the view that these boundaries consisted of a eutectic or minute quantity of impurities existing in the metal, a "fusible and mobile eutectic forming the intercrystalline cement," through which crystal growth was made possible by electrolysis. Since the eutectic is of lower melting point, it exists, at the temperature of crystal growth, in a molten or semi-molten condition. G. T. Beilby²

advances the theory that metal crystals when strained become surrounded with a layer of metal in the amorphous phase, which is tougher and more resistant mechanically than that in the crystalline phase. Recently Rosenhain and Ewen³ have elaborated upon this theory of the amorphous phase and strengthen their argument by experiments in measuring the relative amount of evaporation from large and small grained samples, fired together in a vacuum. They

content varying from 3 to 5 per cent and other impurities reduced to a minimum. A typical analysis before any heat treatment is here given: Si, 3.80 per cent; S, 0.028 per cent; P, 0.010 per cent; Mn, 0.072 per cent; C, 0.050 per cent.

Under the proper conditions of annealing, such a steel will produce grains of enormous size. Fig. 1 is part of a single grain, natural size. The average size of grain is about 25-50 sq. mm. (*cf.* Fig. 1a). Small grains may be produced wherever desired by hammering and subsequent annealing as shown in Figs. 8 and 9. The effect of annealing and mechanical working upon this alloy will be more fully discussed in a later paper.

For most of the work no special polishing was required, merely smoothing up with No. 0 emery and etching with nitric acid. A rapid and efficient etching was obtained by using concentrated nitric acid and alternately dipping and washing the samples, allowing them to remain in the acid only a fraction of a second at a time.

In order to prevent oxidation of the steel samples practically all of them were heated in hydrogen in a platinum wound tube furnace or in an Arsem vacuum furnace. In investigating the growth of grains it was observed that after certain heat treatments the fracture of this alloy was granular, instead of crystalline as under normal conditions. In other words, something had occurred which had weakened the specimen along the lines of the grain boundaries. How then do these boundaries differ from the main mass of metal? Are they merely lines of separation, or are they actual areas, consisting of the metal in a different physical state, or containing some impurity



FIG. 1

find a constant ratio (1.07 to 2.37 for different metals) between their rates of loss in weight.

In studying the properties of silicon-iron alloys the author has performed several experiments which ought to throw some light upon this interesting question. Ordinarily, the study of such problems as these is considerably hampered by the fact that the change in the crystalline grains in metals is too small to follow closely without the aid of a microscope. If we can, in some way, enlarge these grains the problem would become easier to handle. The addition of silicon has been found⁴ to aid greatly in the production of large grains.

DEVELOPMENT OF LARGE GRAIN STRUCTURE

The steel used in these experiments had a silicon

¹ Since this article was written there has come to the author's hands a copy of Humfrey's admirable paper on "The Intercrystalline Fracture of Iron and Steel," Carnegie Memoirs, *Iron and Steel Inst.*, **4**, 80-107 (1912).

² *Phil. Mag.*, **8**, 258 (1904); *Proc. Roy. Soc.*, **79**, 463 (1907).

³ *J. Inst. Metals*, [2] **8**, 149 (1912).

⁴ *Metallographist*, **1**, 325 (1908).

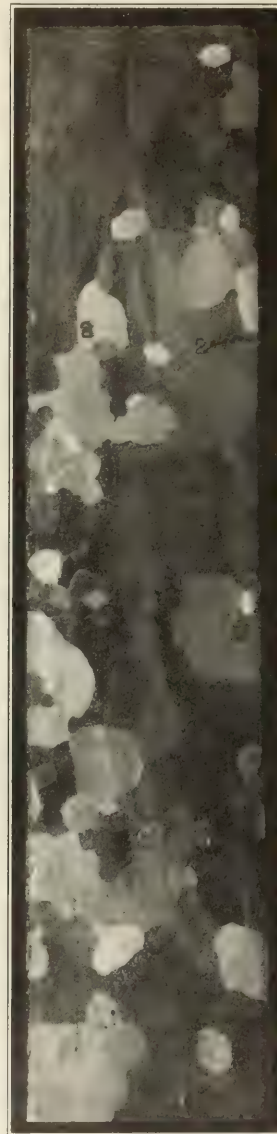


FIG. 1a

thrown out by the crystalline grains in the process of formation and growth?

ETCHING WITH POTASSIUM DICHROMATE

Examination under the microscope gave no indication of the existence of any area of measurable width. Various etching agents were then tried in the hope of obtaining some discriminating agent which would dissolve or reject the material between the grains. Such a result was finally obtained by making the sample the anode in a solution of some oxidizing agent as potassium permanganate, chromic acid, or potassium dichromate. The last named gave the best results.

It was found that when a sheet of this silicon-iron alloy was treated in this way for about 15 minutes, the grains on the end began to drop off, and the whole sheet could be crumbled in the fingers, the grains being perfectly separated at their boundaries. It was soon noted that certain sheets fired in hydrogen did not give this effect, at least not so perfectly, but that sheets fired in nitrogen, air or vacuum seldom failed to give this effect. I say seldom failed, but as a matter of fact there was only one lot of metal that failed. What the difference is between this and the others is difficult to say. Indications are that it is composition, for, if we take a single grain of this kind of metal and form in its center a series of new grains by hammering and heating (*cf.* Figs. 8 and 9), these new grains also are not effected and the metal is as strong as ever, while those made in a like manner in the metal whose grain boundaries were soluble are, like the original ones, caused to fall apart.

The question of the quality and quantity of material removed by the electrolysis naturally followed. Analysis of the solution after electrolysis showed a large amount of Fe present (6.0–7.6 per cent), but this is more than could possibly be accounted for as coming from the boundaries alone. Attempts at analysis of the gases given off, on the assumption that carbon present as carbide in the boundaries would be oxidized in the electrolysis, were unsuccessful.

A further attempt at analysis was made on four samples cut from a single sheet as shown in the sketch.

1	2
3	4

Nos. 1 and 4 were analyzed as a blank, while 2 and 3 were electrolyzed and the separated grains analyzed; the results follow:

	C	Si
Samples 1 and 4.....	0.049	3.856
Samples 2 and 3.....	0.055	3.856

To determine the loss in weight up to the time the sample crumbled, two sheets were carefully cleaned and weighed. These were then electrolyzed. The loss is here shown.

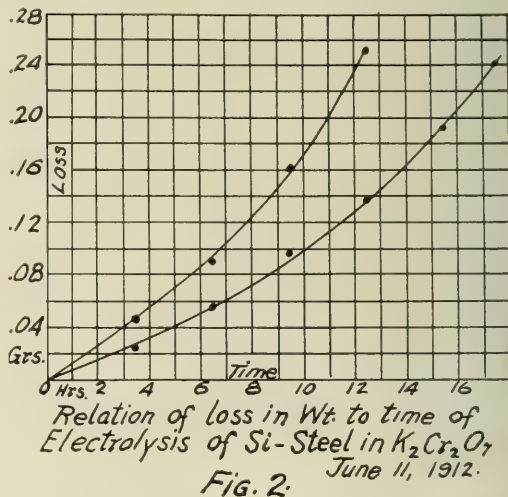
TIME	No. 1, 6.2800 GRAMS, No. 2, 6.5226 GRAMS		CURRENT	
	LOSS		CURRENT	
31 1/2 hrs.	No. 1	No. 2	No. 1	No. 2
3 "	0.045	0.0226	0.218 Amp.	0.155 Amp.
3 "	0.046	0.032	"	"
3 "	0.094	0.0365	"	"
3 "	0.085	0.041	"	"
14 1/4 "	gone	0.0165	"	"
3 "	"	0.058	"	"
2 "	"	0.035	"	"

Total loss till softening (a), No. 1, 0.25 gram (4 per cent).

Total loss till softening, No. 2, 0.26 gram (4 per cent).

(a) By "softening" is meant the point where the last trace of cohesion between the grains disappears, and the sample begins to fall apart from its own weight.

If these figures are plotted on a curve (*cf.* Fig. 2) we find that the loss in weight increases with the 1.3 power of the time. This is probably due to a uniform increase in the dissolving of the grains themselves, or to the weakening of the solution by the iron-chromium compound which separates out as a precipitate.



The concentration of the electrolyte was varied from $\frac{1}{8}$ to 1 saturation and it was found that the rate of solution increased with the decrease in concentration.

It was desirable to ascertain just what width the intergranular lines would assume on continued etching, and two samples were prepared with a backing of soft solder which, it was found, was not attacked by the acid. This solder prevented the piece from falling apart.

The increase in the width of lines was measured with a micrometer eye-piece. The lines at the beginning (during the first 24 hours or so) were very uniform in width. The measurements are here given:

TIME	WIDTH OF LINE	
	No. 1	No. 2
48 hrs.	0.05 mm.	...
60 "	0.07 "	0.09 mm.
72 "	0.086 "	0.12 "
96 "	0.130 "	0.122 "
120 "	0.147 "	0.165 "
144 "	0.184 "	0.183 "
168 "	0.190 "	0.184 "
192 "	...	0.190 "

The action did not cease, however, although it became much slower, as the figures show. The experiment was discontinued because certain of the grains, where measurements were taken, dropped out. Photographs 3 and 4 show the clean cut way in which the



FIG. 3

solution works. The black areas are the places where grains have become loosened and dropped out. It was found in the above experiments that the cross-section of the grains after electrolysis was elliptical, so that there must have been a dissolving away of the edges, thereby widening the spaces more than the "space" material would justify.

Mechanical cracks of various kinds were made in the material to see if the mere junction of two surfaces would cause similar electrolytic attack, but in no case were these cracks affected in the least.

The polished surfaces of the grains remained after lengthy treatment, and there was no sign of attack except at the boundaries. The chromic acid appeared to hold them entirely passive.

Assuming then that the attack was caused by the foreign material present between grains, it was decided to try the effect upon discs of *cast* metal. Here we have large grains but the sudden cooling might not allow the impurities time to diffuse out of the grain. The photographs 5A and 5B show the results obtained.

Fig. 5A shows an unannealed cast disc treated with $K_2Cr_2O_7$ by electrolysis. In this sample the whole

surface is pitted with small cavities about 0.08 mm. in diameter on the average, and about 0.15 mm. apart. The surface of the metal is also discolored. Around the grain edges, however, there is a bright band, varying from 0.25 to 0.50 mm. in width, which is almost entirely free from any marking whatever.

From these grain edges, in practically every grain, start tiny fissures which run back into the grain for about 0.2–0.5 mm. These fissures are evidently along crystal edges, for they run in parallel straight lines, varying in direction in the different grains.

5B is a contiguous section of the same casting treated in the same way, but having first been annealed. In this sample the grain surfaces were untouched, and only the boundary lines had been attacked.

These experiments seem to indicate that there is some chemical change in the grains themselves during anneal, that is to say, before annealing, the material cooled so quickly that the impurities had no time to migrate to the grain boundaries except those very near (*cf.* 5A). After this piece is annealed, however, we

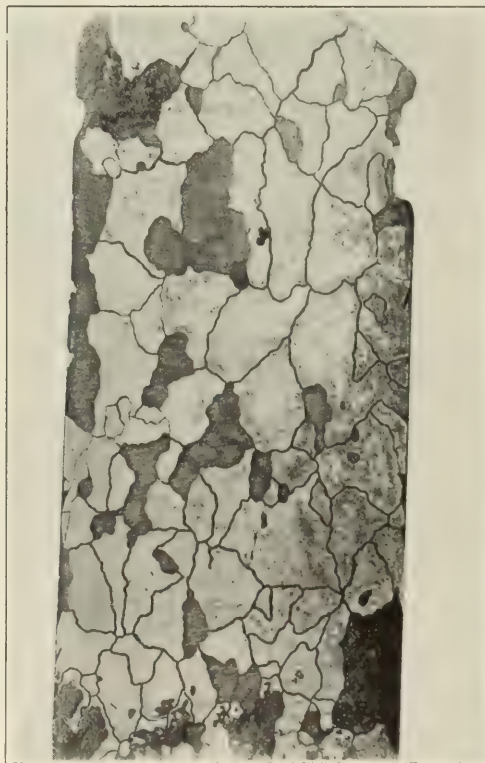


FIG. 4

have no evidence of action on the surface of the grains, only at the boundaries.

HYDROGEN TREATMENT

By treating a bar of this material in dichromate the grains could be readily separated, as shown in photo-

graph 6. In this way large masses of material making up a single grain, could be isolated.

Following up the results noted in the beginning of this work, namely, that heating to a high temperature in hydrogen near the melting point seems to cause a fusion between grains, and a decided weakness, I tried a large number of bars in different atmospheres and at different temperatures, to ascertain what the conditions were that caused this weakening of the boundary lines between grains. It was found that when a bar or sheet is heated to 1400°C . in hydrogen for about 8 hours it becomes very brittle, and the grains may be separated by hammering the specimen. A $1/4$ -inch rod so treated, broke into several pieces just by dropping 3 feet to a wooden floor, and when hammered lightly the grains were readily separated.

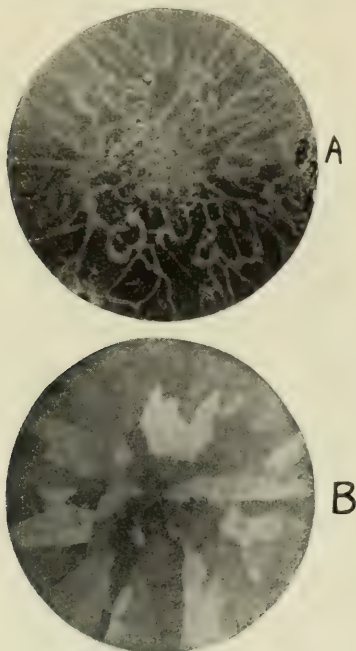


FIG. 5

It was also observed that this intergranular brittleness was not obtained under 8–10 hours on large bars $1\frac{1}{2} \times \frac{1}{2}$ inch cross-section, while on the $1/4$ -inch rods it was obtained in about an hour. Photograph 7 shows a granular (I) and a cleavage (II) fracture.

The time factor together with the $\text{K}_2\text{Cr}_2\text{O}_7$ experiments led us to believe that the action of the hydrogen must be of a chemical nature, and several other experiments suggest themselves whereby this theory might be proved or disproved: *First*, Does any other gas give the same result? *i. e.*, is it a temperature effect? *Second*, If something is removed can it be restored again, and if so, will this restore the toughness of the metal? *Third*, If something is removed, then the composition of the "cement" is changed, and it is a question whether the chromate electrolysis will then fail to separate the grains.

In answer to the first two questions, eight bars were heated at different times to the same temperature (above 1400°C .) as those treated in hydrogen. Some of these were heated in air, and others in air freed from oxygen, but in no case was the fracture changed from the original cleavage fracture.

I then fired a bar in hydrogen, to obtain this weak intergranular condition, and then, assuming that the

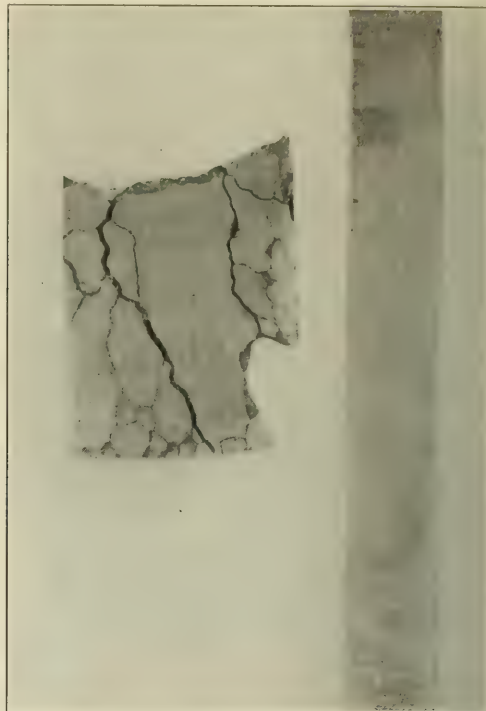


FIG. 6

"cement" was carbide which had been destroyed on heating, refired in hydrogen containing a hydrocarbon vapor. This refiring was done at the same temperature and time as in the original treatment. When

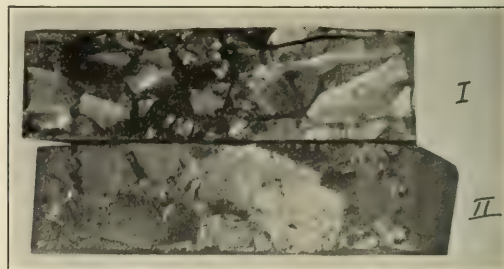


FIG. 7

tested after this treatment it was found that the sample was as strong as it had been originally, and the fracture was now across the grains instead of along the boundaries.

Ten or more repetitions of the experiment were made at different times, varying the conditions and samples, etc., but always with the same result, *viz.*, the "cement" material weakened by the hydrogen was always returned to its original toughness by the hydrocarbon treatment, the piece then always splitting across the grains and never at the grain junctions. Moreover, the same sample could be reverted from one condition to the other at will and as often as desired.

Another experiment points very strongly to the theory that something is removed by the hydrogen treatment. If a bar which has been treated in this manner so that the grains are readily separated on hammering, is soaked in molten copper at about 1200°C . for an hour or so, it is found that the copper has diffused into the bar between the grains, and that every grain is covered with a very thin coating of copper. This could not be done with material having a cleavage fracture.

In answer to the third question, we had already observed that some hydrogen-fired samples (possibly those heated at low temperatures) did not separate on the grain boundaries when electrolyzed in chromate solutions. Numerous experiments were subsequently tried in the light of these other experiments and they all showed the same results; namely, that samples, which had a cleavage fracture and would readily fall apart at the grain junctions if electrolyzed in chromate, would not, after having been so treated as to

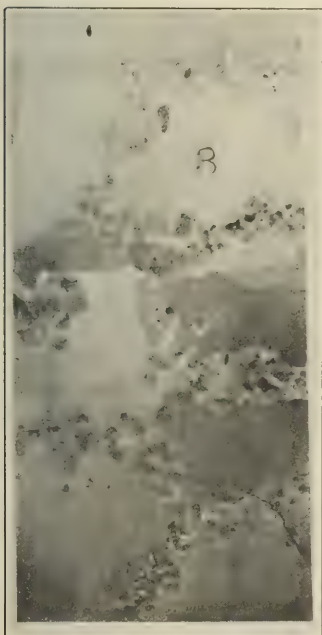


Fig. 8

give a granular fracture, show any effect at all when electrolyzed in $\text{K}_2\text{Cr}_2\text{O}_7$. The reverse, however, is not always true, *i. e.*, all samples which do not separate by the chromate treatment have not, of necessity, intergranular brittleness (only one or two samples).

It will be seen then that all of these experiments seem to indicate that the chemical theory is the correct one. One other experiment, however, seems to make this conclusion still somewhat doubtful. When a sheet has been annealed to 1350°C . or so, and the large grains form, according to the above assumption the impurities have been thrown out of the grains. Now, if inside one of these large grains

smaller ones can be produced (*cf.* Figs. 8 and 9), these should show no separation when electrolyzed in the chromate solution. This was tried on three samples, and in every case the secondary grains

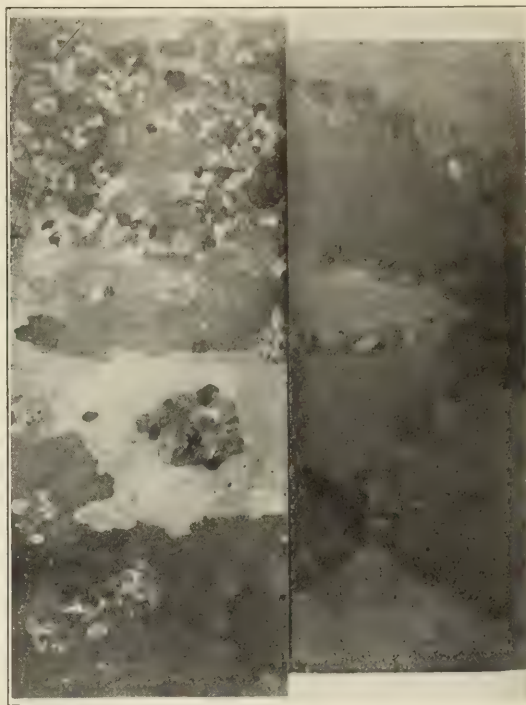


Fig. 9

dropped out as well as the original ones. This argues rather against the theory that there is a chemical difference between the grains and the boundary lines, unless we assume that there has been some impurity absorbed from the gases during annealing. This is quite possible, considering that the strained portion must have contained quite a little of the more active 'amorphous phase.

RESISTIVITY MEASUREMENTS

By drawing this iron-silicon alloy out into a wire (0.02 inch) it was possible to obtain pieces containing comparatively few grains along its length. Most of the grain junctions extended right across the wire, so that compared with the fine-grained material, an electric current has much fewer junctions to pass through. If the cement has any different resistance than the grain material then it should show up in resistivity measurements.

A series of ten measurements was made and resistances taken: (1) as drawn, (2) annealed at 800°C ., (3) annealed at 1350°C . The results showed an average of 3 per cent increase in resistance for the 800°C . anneal, and a subsequent 15 per cent decrease, from the original value, for the large-grained samples. An attempt to calculate the resistivity of each boundary by counting the number proved fruit-

less, because of the existence of a large number of grains that did not run all the way through.

The increase at 800° C. is unusual, because in most metals the resistivity is lowered by annealing. If we consider the results entirely from a point of view of the number of grain boundaries along the length of the wire, we would expect a slight rise in resistivity, owing to the fact that in the unannealed state the grains are drawn out, and so present fewer boundary lines along the length of the wire than when subsequently annealed. If the change in resistivity were due wholly to the presence or absence of the amorphous phase then we would expect the usual decrease in resistivity after the first anneal.

When heated in a high vacuum the cement apparently volatilizes more rapidly than the metal grains, and leaves deep fissures between the grains. Such an experiment, using pure silver, is given by Rosenhain and Ewen as proof that the cement was amorphous silver, but it is readily conceivable that any foreign substance present may also have a lower vapor pressure and give the same result. We also obtained like results with wrought tungsten.

Although the facts seemingly indicate that carbon, either free or combined, is the cementing material, all attempts to etch out the Fe_3C from a cementitic steel by electrolyzing in chromate have failed. A piece of "burned" steel containing a smaller proportion of cementite, similarly treated, separated nicely on the grain boundaries. Commercially pure ingot iron is not attacked, while iron containing a high percentage of free carbon is rapidly dissolved.

Analyses were made of samples from a bar: (1) as rolled, (2) fired in hydrogen to 1325° C. to a partially granular fracture, (3) fired to 1425° to a complete granular fracture, and (4) refired in hydrogen over hydrocarbon till it reverted to a cleavage fracture. The results gave no indication that any of the impurities (S, P, C or Mn) had been removed or reduced by any of these treatments, with the exception of carbon, which was reduced from 0.065 per cent to 0.013 per cent on the first heating in hydrogen. The carbon content, however, did not go up again on heating with dilute hydrocarbon vapor.

The proof that this material is carbide or any other of these impurities is still indirect, but on the other hand the assumption that the cement is only the amorphous phase of either metal or of the solid solution is in view of these experiments insufficient. If we assume that this is the case, we would expect this amorphous material to exist in all samples, and moreover, once destroyed by heat we would hardly expect it to be restored on reheating to the same temperature in a slightly different atmosphere, and this change reversible indefinitely without the least change in size or shape of the grains. On the other hand, the assumption that these boundary lines hold certain impurities explains most of the facts observed, for then the action of the hydrogen partakes of a chemical nature, and the reversing of the physical state is due to the addition or subtraction of some specific element whose presence or absence determines

the strength of the junction. The experiments with samples of cast metals also strengthen this view, and when the metal is fused in pure hydrogen the old grain boundaries vanish, while the new ones are not attacked by the chromic acid, owing to the removal of the impurity.

These experiments, it will be remembered, have all been performed upon a product having only a commercial degree of purity, and the existence of sufficient impurity in highly purified metals may be questioned, but the amount required is so small that it would be difficult to obtain a metal sufficiently pure.

SUMMARY

It has been shown that the intergranular cement in a 4 per cent silicon-iron alloy may be completely removed by making the alloy the anode in a solution of potassium dichromate, and also by firing in hydrogen to a temperature just below the melting point. It is again replaced in the latter case by firing in a dilute hydrocarbon vapor.

It is shown that in the unannealed cast metal impurities exist throughout the mass of the grain, and not only at the boundaries, while after annealing these impurities have passed to the boundaries. Resistance measurements on large and small grain wires show that the "cement" has a higher resistance than the crystalline metal.

In view of the facts it does not seem sufficient to say that the intergranular cement is composed entirely of the grain substance in the amorphous phase, but rather that it consists of the metal in combination with certain impurities which have been rejected by the crystalline grains.

It is not the purpose of this paper to deny any existing theory regarding the composition of the intergranular cement in metals, for the author realizes its limited scope, but it is hoped that the facts observed may aid somewhat in the general investigation of this subject.

RESEARCH LABORATORY
GENERAL ELECTRIC COMPANY
SCHENECTADY

INFLUENCE OF VARIOUS ELEMENTS ON THE CORRODIBILITY OF IRON¹

By CHARLES F. BURGESS AND JAMES ASTON

Incidental to an extensive investigation on electrolytic iron and alloys produced therefrom, as carried out under a grant made a number of years ago by the Carnegie Institution, tests were made upon the corrodibility of a number of alloys. Acknowledgment is made to Mr. B. F. Bennett for his assistance on this particular phase of the work.

The electrolytic iron which has been used as a basis for the alloys, when compared to materials commercially available, may be taken as essentially pure and in making up the alloys care was taken to exclude impurities as far as possible. The method of preparing the test samples consisted, first in melting the electrolytic iron or the electrolytic iron alloy in closed graphite magnesia-lined crucibles heated in an elec-

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

trical resistor furnace. Upon cooling down the small ingots weighing from one to two pounds were forged

into rods and strips. Only those alloys which would forge readily into shape were included in these tests.

From the forged bars, samples were taken for chemical analysis and through the courtesy of Messrs. Booth Garrett and Blair, of Philadelphia, the determinations given in the first column of the attached table were obtained.

The corrosion test samples were cut to a size of about $2'' \times 1'' \times \frac{1}{8}''$ thick (5 cm. \times 2.5 cm. \times 3.1 mm. thick). They were exposed to the weather conditions in Madison, Wisconsin, for a period of 162 days, from July, 1909, to February, 1910. Before exposure, all samples were ground to a uniformly smooth surface. After the removal of rust by the ammonium citrate method, all samples were subjected to an accelerating acid corrosion test, using a twenty per cent sulfuric acid, and immersing for a period of one hour. Each sample was suspended by itself in a beaker to avoid errors by presence of other material.

Some results of interest were derived from these tests, though how far they may be of practical value as indicating the influence of various elements on commercial material is problematical. The materials used are practically carbon-free as well as having such minor quantities of sulfur, phosphorus, silicon and manganese (except where intentionally added) as to have in all probability little effect. There is widely prevailing belief that the effect of any element added to iron is to increase corrodibility by furnishing galvanic couples. A great majority of these test samples indicate the reverse; that is, a greater durability for the alloys than for the electrolytic iron base.

Comparisons between the corrodibility of electrolytic iron and certain forms of pure commercial iron on the market indicate that electrolytic iron is more corrodible both in the atmosphere and in acids. In fact no quantitative comparisons have been attempted as between the alloys produced in this investigation and commercial materials. As an approximate indication, however, ranges are given for tests on commercial materials at the bottom of the table for the experimental alloys.

ELECTROLYTIC IRON

The electrolytic iron for which data are given in the table is not introduced as a sample of the purest that can be made but rather the average material, being a good representative standard for comparison. As a matter of fact, during the course of the tests, as will be noted at the foot of the table of data, figures were obtained upon various grades of iron and steel of commercial grade and of widely varying degrees of purity; and in these results may be noted values of corrosion both higher and lower than those of the electrolytic iron sample.

So far as this particular sample is concerned it shows nothing especially striking in resistance to corrosion either in acid or in the atmosphere.

In the acid test in particular it does not fall in line with the commonly accepted view that a close approach to purity would indicate a high resistance to acid attack. On the contrary this particular material has

	ATMOSPHERIC CORROSION			
	ACID CORROSION		Lbs. per sq. ft. per year	Kg. per sq. meter per year
	Per- centages	Gram per sq. dm.		
Electrolytic iron.....		1.300	0.1025	0.499
Aluminum.....	0.067	0.628	0.110	0.513
	1.333	0.760	0.080	0.390
Arsenic.....	0.292	0.448	0.0830	0.405
	0.430	0.815	0.0703	0.343
	0.915	0.405	0.0870	0.425
	1.810	0.131	0.0720	0.352
	3.862	0.086	0.0640	0.312
	4.141	0.102	0.0740	0.361
	3.562	0.144	0.0630	0.306
Cobalt.....	1.035	0.705	0.049	0.239
	2.000	1.020	0.070	0.342
	4.055	0.356	0.042	0.205
	5.052	0.257	0.042	0.205
Copper.....	0.089	0.178	0.052	0.254
	0.202	0.095	0.039	0.190
	0.422	0.059	0.055	0.268
	0.592	0.112	0.050	0.234
	0.804	0.104	0.053	0.259
	1.006	0.067	0.046	0.225
	1.510	0.147	0.046	0.225
	2.005	0.091	0.051	0.249
	3.990	0.093	0.035	0.171
	5.070	0.087	0.031	0.151
	6.160	0.143	0.041	0.200
	7.050	0.186	0.033	0.161
Lead.....	0.061	1.300	0.056	0.273
Manganese.....	0.505	0.560	0.055	0.268
	1.000	0.520	0.080	0.390
	2.000	0.725	0.062	0.302
	3.000	1.110	0.067	0.327
	10.419	0.352	0.089	0.435
Nickel.....	0.270	0.6330	0.059	0.288
	0.560	0.5470	0.071	0.347
	1.070	0.5070	0.058	0.283
	1.930	0.1920	0.023	0.112
	7.050	0.2260	0.038	0.185
	8.170	0.1250	0.029	0.141
	10.200	0.0910	0.027	0.132
	11.290	0.1230	0.027	0.132
	12.070	0.0840	0.024	0.117
	13.010	0.2370	0.031	0.151
	19.210	0.0720	0.018	0.088
	22.110	0.0254	0.020	0.098
	25.200	0.0540	0.023	0.112
	26.400	0.5540	0.021	0.102
	28.420	0.1550	0.021	0.102
	35.090	0.1830	0.018	0.088
	47.080	0.1600	0.0126	0.062
	75.060	0.0490	0.0044	0.0215
Selenium.....	0.017	0.190	0.1385	0.676
Silicon.....	0.233	1.630	0.104	0.509
	1.190	1.190	0.076	0.370
	1.033	0.850	0.106	0.518
	1.897	0.800	0.124	0.606
	2.826	1.270	0.130	0.635
Silver.....	0.281	1.020	0.065	0.317
	0.492	1.760	0.090	0.430
	0.581	1.340	0.073	0.356
	0.691	1.170	0.092	0.450
Tin.....	0.288	0.284	0.069	0.337
	0.342	0.350	0.039	0.190
	0.686	0.386	0.049	0.239
	1.568	1.030	0.058	0.283
Tungsten.....	0.406	0.363	0.076	0.371
	0.925	0.088	0.062	0.302
	2.334	0.086	0.062	0.302
	3.553	0.332	0.063	0.308
	5.982	0.304	0.060	0.293
	9.849	0.398	0.040	0.195
	13.641	0.365	0.049	0.239
	23.866	0.183	0.044	0.215
Commercial grades:				
Various grades of low carbon iron and steel			0.300 to 0.73	
High carbon steel			0.278	
Cast iron—scale removed			0.770	

been attacked even more severely than most of the alloy samples tested at the same time.

ALUMINUM

In this series there is not enough data to warrant conclusive deductions. So far as the sample with 0.067 per cent of aluminum is concerned this may be taken as corresponding to iron free from alloying agents. The second sample carrying 1.33 per cent of aluminum shows an even higher attack by acid than the one of the lower aluminum, but there has been a slight falling off in the atmospheric corrosion. However, there has been nothing striking in either case.

ARSENIC

In view of the fact that the presence of small amounts of arsenic in sulfuric acid pickling solutions decreases markedly the rate of the attack, it has been suggested frequently that arsenic present as an alloying constituent of steels might make such steel more resistant to corrosion, particularly to acid corrosion. This, however, appears to be an erroneous assumption as increased corrosion in acid has been noted by Heyn and Bauer and by Berthier. No satisfactory or conclusive work seems to have been done on the resistance of these materials to atmospheric influences.

Our results cover a series in which the arsenic ranges from 0.29 to 3.56 per cent and we find a fair resistance to the acid attack, which resistance falls off appreciably with increase of arsenic content. On the other hand the corrosion in the atmosphere is somewhat on a par with that of the electrolytic sample, and there would seem to be no particular merit in the use of arsenic alloys for resisting atmospheric corrosion.

From the point of view of physical qualities, also, this series would not be of particular merit, since the brittleness and weakness resulting from the addition of arsenic would be serious. Addition of arsenic seems to result in high magnetic qualities, but it is an element which is difficult to add, and if of service from the corrosion point of view it would have to be added in very large amounts and there would thus result a structurally or mechanically poor material.

COBALT

In view of the close relationship in the general properties of cobalt and nickel, it might be natural to expect that the use of these elements as alloying agents would result in somewhat similar properties. The series here tested, however, in which the cobalt varies from 1.3 to 1.5 per cent does not point to any close relationship. The resistance to acid of this series is not particularly striking but does fall off appreciably with increasing cobalt content. The same general effect is noted in the atmospheric tests; but while the corrosion is fairly low, there is not the same resistance to atmospheric attack as is obtained by the addition of the same quantity of nickel. This series shows a fairly close relationship in the rates of atmospheric and acid attack.

To use cobalt for the purpose of making a material highly resistant to corrosion would seem to demand

considerable quantities of this element. There would be no advantage, therefore, in the use of this metal as compared with nickel, in view of the high relative cost of the cobalt.

COPPER

The influence of copper upon the corrosion of iron and steel, and to some extent as well, upon the other physical properties is, at the present time, a matter of controversy. So far as the resistance to acid attack is concerned, particularly to sulfuric acid, the evidence seems to be convincing that copper additions result in marked decrease in the rate of such attack. There is a tendency also, not supported by conclusive tests, to believe that copper additions will likewise increase the resistance to atmospheric corrosion.

The series herein tabulated, in which the copper ranges from 0.089 to 7.05 per cent have the expected high resistance to acid attack and also show a low corrosion in the atmosphere. The latter is of particular interest, inasmuch as the values are consistently low throughout the series and the markedly beneficial results seem to be obtained from even small amounts of added copper.

In view of the materially improved physical properties resulting from one to two per cent of copper additions, together with the low cost of such addition and the corrosion resistance herein noted, it would seem that this series is of particular promise and worthy of extended study. The quality, both mechanically and from the corrosion point of view, is entirely comparable with that resulting from the use of corresponding amounts of nickel and, of course, there is a materially lessened cost for the addition.

The exact reason for the decreased corrosion is somewhat a matter of speculation. Considering that iron and copper form solid solutions, at least up to three per cent or thereabouts of copper addition, or well within the limits of commercial utility, we should expect the structure of resultant alloy to be one of perfect homogeneity. There should, therefore, be no internal influence tending to promote increased electrolytic action, and the effect of the dissolved copper should at the very worst be only neutral as far as corrosion is concerned. In fact, increased resistance to corrosion might be expected, since the solid solution of the two elements might decrease the solution tendency of the iron; or if the iron finally goes into solution it may leave a deposit of copper forming a film and protect the underlying metal from further attack. The presence of such a copper film has been observed repeatedly in the course of etching of samples for microscopic examination and has been noted by other investigators during acid attack of copper-iron alloys. This speculation seems to be confirmed by the tests herein enumerated.

LEAD

But one alloy of this series was tested and that contained only 0.061 per cent of this element. The acid corrosion is the same as that observed by the electrolytic iron while the atmospheric corrosion has dropped to about half the figure of electrolytic iron.

Not enough data are at hand, however, to warrant any deductions regarding the influence of lead upon the corrosion of iron.

MANGANESE

The supposedly increased corrosion of modern steels as compared with the older iron has generally been ascribed to the presence of the manganese which occurs in the latter day materials as a result of modern process of manufacture. It may be, however, that the manganese is blamed for results due to other elements associated with it, or perhaps to other factors resulting from modern conditions of manufacture.

So far as our tests show in this series, which runs from 0.50 per cent manganese to 10.42 per cent manganese, there is nothing worthy of particular comment either in the acid or atmospheric corrosion. There is considerable inconsistency in the results and the atmospheric tests in particular seem to indicate a slight increase of corrosion with increase of manganese content, though in all cases the corrosion was less than for the electrolytic iron alone.

The alloying relations in this series are those of solid solution, in this respect similar to the copper-iron alloys in the useful range. We have, therefore, a homogeneous structure and no internal causes for electrolytic action. However, in view of the very similar properties of the two metals there would probably result but little change in the solution tendency of the alloy as compared with the iron itself. Also there would be no deposition of a protective film as was mentioned in the copper series, since manganese is attacked very much like iron and would rust away in a similar manner. Consequently rust once formed from solution of either metal should aid, rather than retard further progression of the corrosion.

NICKEL

This series shows alloys notably good both in the acid and atmospheric tests. There is a general tendency for increased resistance with increased nickel content.

In the region of nickel content, such as is used in practice, about three per cent, we note a marked falling off in the atmospheric corrosion. The hindrance to the general use of this property is the relatively high cost of the nickel addition, and it would seem that these alloys would not offer particular merit unless the use of the material is also warranted by the increased strength resulting from the addition. The highest resistance noted lies well up in the series; that is, at ten per cent nickel and above. Such alloys would be beyond the range of general commercial utility, not only because of the high cost of the nickel but because of the hardness and brittleness and generally disadvantageous physical properties in this region of the series.

The alloying relations of the nickel and iron are those of solid solution, and it would seem that the protective effect is due perhaps to the same reasons cited in the case of the copper-iron alloys; that is, we would have very probably a markedly decreased solution tendency, and in case of any corrosion it would result in a solu-

tion of the iron and the consequent concentration of the nickel as a surface protecting film.

SELENIUM

There was tested but one alloy in this series with the very low content of 0.017 per cent of selenium, consequently no particular deductions can be drawn. The acid resistance in this particular sample is very low while the corrosion in the atmosphere is noticeably high.

SILICON

In this series the silicon content varied from 0.23 per cent to 2.82 per cent. The corrosion values are in general high and somewhat conflicting. In fact, this series seems to have suffered the greatest corrosion noted. There has been a general tendency for increase in the atmospheric corrosion with increase of silicon content but not a very material increase.

There seems to be an inclination to assume increased resistance to corrosion in the silicon steels, but the only reliable data appears to be that obtained upon acid tests and mainly upon acid tests of the alloys of high silicon content. Here a compound of iron and silicon becomes the principal constituent and the resistance to acid is probably due largely to this.

So far as ordinary amounts of silicon are concerned its use seems to be disadvantageous both in acid and atmospheric corrosion. Also, silicon behaves much like arsenic, and while it results in good magnetic qualities the resultant steels are otherwise poor physically, being brittle, weak and hard to work.

SILVER

Although alloys were made in which the added amount of silver was as high as 10 per cent, the resultant alloys actually indicated a maximum of 0.69 per cent retained, and the series here cited has a silver content varying from 0.28 per cent to 0.69 per cent. There is no particular merit in this addition so far as either acid or atmospheric corrosion is concerned, and all of the figures are closely comparable to that obtained with electrolytic iron alone. There is of course no particular commercial significance attached to the use of iron-silver alloys because of the relatively high cost of the addition.

TIN

This series has a tin content varying from 0.28 to 1.56 per cent. In the lower end of the series the resistance to acid attack is particularly good but the corrosion in acid increases perceptibly with the higher content of tin. As far as the atmospheric tests are concerned there is nothing of particular moment. There is a slight falling off, however, with increase of tin.

The iron-tin alloys are somewhat similar in their general properties to the iron-arsenic and iron-silicon alloys—that is, all of these additions result in improved magnetic quality of material but at the expense of the physical, and the resulting alloys are brittle and weak and hard to work.

TUNGSTEN

The tungsten varied from 0.40 to 23.86 per cent.

In the acid test the results are all good, some of them very strikingly so; but there is a general irregularity in the figures. The same is true in regard to the atmospheric tests with a seeming tendency towards decreased corrosion with increased tungsten content.

However, the general results are not especially worthy of attention and considering the fact that any markedly decreased corrosion is obtained only after high tungsten additions, these alloys do not offer special value from the corrosion standpoint, since with the high tungsten additions we are entering the tool steel range of alloys of high cost and extreme hardness and brittleness.

CONCLUSIONS

These tests covering several series of alloys of iron with other elements do not seem to point to any quantitative relations as between the acid and atmospheric corrosion.

So far as the atmospheric tests are concerned, numerous alloys can be noted in which the corrosion is less than in the electrolytic iron. The copper series would seem to offer particular advantages in view of the beneficial results obtained with small copper additions and because of the consistently low values throughout the series. Again these benefits are obtainable without prohibitive cost for the addition agent.

UNIVERSITY OF WISCONSIN
MADISON

CHARACTERISTICS AND DIFFERENTIATION OF NATIVE BITUMENS AND THEIR RESIDUALS¹

By CLIFFORD, RICHARDSON

The native bitumens occur in such varied forms and for any particular form, such as petroleum, are of such varied character that their accurate characterization and differentiation are much to be desired. It is a notable fact that in each new field developed, a type of petroleum is found which differs in some respects, often important, from those which have been previously known. There are, at least in the Western Hemisphere, no two fields which produce oils of identical character, although similarities exist. This fact is particularly emphasized by the peculiar differences in the heavy petroleum from the California, Mexican and Trinidad fields. The oils from Mexico and Trinidad resemble none with which we have previously been acquainted and differ from one another as strikingly as from other similar heavy petroleum, such as that found in California, especially as regards the manner in which the sulfur, which is found in considerable amounts in both of them, is combined and the behavior, on this account, of the two oils on distillation. A study of the relation of these petroleum and their residual products to each other and to other well-known forms of native bitumen is of interest.

Some of the important considerations in characterizing the native bitumens are the determinations of the series of hydrocarbons of which they are composed, whether they consist of paraffine hydrocarbons,

to any and to what extent, what proportion of the hydrocarbons are saturated—that is to say, not removed by strong sulfuric acid on treatment with that reagent; how much sulfur the bitumen contains and, in the case of petroleum, whether and to what extent it is removed by steam during distillation and what percentage of residual coke, ash-free, they yield on ignition in absence of air when the ignition is carried out by a conventional method. Of course, there are other physical and chemical properties which characterize the various forms of bitumen, but they are not of the same value for purposes of differentiation as those which have been mentioned. To these may be added a study of the possibility of handling the particular bitumen industrially, so that uniform results may be obtained and the products always be, with due care, of uniform character.

With the view to making a comparative study of the character of the various native bitumens which are available in the United States in 1913 and differentiating them on such a basis, the accompanying data (Tables I to VI) have been collected from previous publications of the writer and from recent analyses made in this laboratory under the direction of Mr. C. N. Forrest.

With these data available, the various forms of native bitumen which have been examined can be characterized and differentiated and, in connection with their behavior under treatment by industrial processes and under service tests and in highway construction, their value for the latter purpose may be determined.

FLUXES

The materials which have been denominated fluxes in the accompanying table are the residuals left after the removal by distillation of the more volatile fractions of various petroleum, until the product is of such a density that it contains little or nothing volatile on heating 50 grams for 5 hours at a temperature of 325° F. They consist of viscous oils of a character used for fluxing solid asphalts or for direct application to road surfaces as a carpet coat.

Paraffine Fluxes.—The residuals derived from the paraffine petroleum are characterized by containing hard paraffine scale, from 14.5 to 4 per cent, consisting to a predominating degree of saturated hydrocarbons, 85.6 to 74.1 per cent, and having a specific gravity, normally, of 0.92 to 0.94. Those derived from the paraffine oils of Ohio and Pennsylvania, as long ago as 1898, and not available commercially to-day, consisted of over 80 per cent of saturated hydrocarbons. They yield but a small percentage of residual coke and, with the exception of the Ohio residuum of 1898, contain but little sulfur.

In this classification there is included a Russian residuum which, although it contains no paraffine scale, consists largely of saturated hydrocarbons, and a shale oil from France which, although the amount of saturated hydrocarbons that it contains is much smaller than is found in the paraffine petroleum residuals, is of a paraffine nature, as shown by the paraffine scale present.

¹ Also published in the *Engineering Record*, 67, No. 14, 466 (April 26, 1913).

These residuums are of no value as binders for highway construction other than for fluxing the native asphalts and are unsuitable even for this purpose, with other solid bitumens not true asphalts, such as gilsonite and grahamite. The data in regard to the paraffine fluxes are of value for comparative purposes.

Semi-Asphaltic Fluxes.—The semi-asphaltic fluxes are differentiated, primarily, by a higher density than those derived from paraffine oils, 0.95 to 0.97. They contain a much smaller amount of paraffine scale and approach very nearly in the amount of saturated

Mexican Fluxes.—There is one other flux—that produced from Mexican petroleum—which differs from those of either of the other classes. It is differentiated from them completely by marked characteristics, such as the fact that it carries a high percentage of sulfur, yields a high residual coke, ash-free, contains 2 per cent or more of hard paraffine scale, while only 80 per cent of it is soluble in 88° naphtha, as compared to over 90 per cent in the case of the other residuums. As far as the density and percentage of saturated hydrocarbons are concerned it might be regarded as an asphaltic flux, but because of its other characteristics it must be

TABLE I ANALYSES OF RESIDUAL FLUXES

TEST NO.	IDENTIFICATION	Specific gravity	Per cent pure bit. sol. in 88° naph.	Per cent pure bit. as sat. hydrocarbons	Paraffine scale	Sulfur	Residual coke, ash free
<i>Derived from paraffine petroleum</i>							
30,485	Russia, 1896.....	0.910		79.3	0.0		
	Penna., 1899.....	0.913		85.6	14.5	0.6	
	Ohio, 1898.....	0.924		81.9	8.5	2.6	4.0
75,272	Ohio, 1904.....	0.922	99.4	78.3	9.6		
69,731	West Va., 1904, Ky. crude.....	0.940	96.5	85.0	10.3		
	Canada, 1905.....	0.937	96.9	78.0	8.1		
84,255	Corsicana, Tex., 1906.....	0.940	95.6	83.1	4.0		
100,537	Lima, Ohio, 1907.....	0.943	97.3	75.1	6.4	0.44	2.8
100,610	Whiting, Ind., 1907.....	0.930	96.6	75.3	7.9	0.50	1.9
100,446	Neodesha, Kan., 1907.....	0.926	97.4	74.1	8.9	0.61	1.8
65,402	Shale oil, France.....	0.985	93.6	43.6	4.4	tr.	3.0
<i>Derived from Mexican petroleum</i>							
37,996	Mexican, 1912.....	1.007	79.9	43.2	2.0	4.3	10.0
<i>Derived from semi-asphaltic petroleum</i>							
66,364	Beaumont, Tex., 1903.....	0.974	95.2	79.4	1.7		3.5
68,265	Beaumont, Tex., 1903.....		96.3	67.9	0.3	0.74	2.8
69,330	Beaumont, Tex., 1904.....	0.957	97.5	72.8	1.0		3.0
75,260	Beaumont, Tex., 1904.....	0.952	99.1	72.3	1.0		
81,159	Texas, 1905.....	0.961	96.9	80.6	2.1		
84,762	Chaison, Tex., 1906.....	0.962	94.9		4.6		
<i>Derived from asphaltic petroleum</i>							
68,489	California, No. 2, 1903.....	1.002	92.4	47.9	0.0		6.0
69,607	California, "G" grade, 1904.....	1.006	92.3	41.8	0.0		6.0
39,143	Trinidad, 1912.....	1.004	86.9	35.3	0.0	2.6	7.0

TABLE II—ANALYSES OF CONDENSER BLOWN OILS

TEST NO.	IDENTIFICATION	Penetration	Ductility	Bit. sol. in CS ₂	Per cent pure bit. sol. in 88° naph.	Per cent pure bit. as sat. hydrocarbons	Paraffine scale	Sulfur	Residual coke, ash-free
71,647	Pittsburgh flux.....	38	None	97.6	66.1	55.5	3.7	4.75	13.7
71,436	Hydrolite "B".....	55	None	99.9	67.9	64.2	1.0	0.56	12.2
114,578	Hydrolite "B".....	41	None	99.8	71.0	57.0	1.0	0.41	8.7
112,167	Calif. Obispo, 1909.....	25	7 3/4 cm.	99.6	61.5	35.7	0.1	1.22	17.3
127,455	Calif. Obispo, 1909.....	11	2 1/2 cm.	99.6	63.4	38.2	0.3	1.23	19.6
122,860	S. O. Co. binder No. 3.....	85	3 1/2 cm.	98.8	74.9	44.3	1.0	0.77	13.2
125,173	S. O. Co. binder "B".....	135	29 cm.	99.8	76.1	51.7	3.1	0.68	12.6
122,134	Gulf binder.....	35	6 cm.	99.4	70.1	48.4	0.2	0.71	14.6

hydrocarbons which are present to the paraffine residuums. They are sharply differentiated by the fact that they will satisfactorily dissolve and flux such solid bitumens as gilsonite and grahamite.

Asphaltic Fluxes.—The asphaltic fluxes are differentiated from the previously mentioned classes by a still greater density, nearly that of water, by the absence of hard paraffine scale and by the fact that the unsaturated hydrocarbons predominate. They yield a larger amount of residual coke, ash-free, on ignition than other fluxes. Those from California petroleum differ from that produced from Trinidad oil by containing less sulfur. It appears that the three classes of fluxes are distinctly differentiated.

classified by itself, more especially on account of the hard paraffine scale which it carries, which points to the presence of paraffine hydrocarbons, and because of the behavior of the crude oil in which it originates on distillation.

CONDENSED OR BLOWN OILS

For some time there have been upon the market bitumens prepared from the residual fluxes by treatment with sulfur or air at high temperatures. They are short or lacking in ductility and cheesy or non-adhesive. The data which are available in regard to these materials show that the effect of such a treatment is to produce a material which may be regarded as dehydrogenated and condensed as far as its molec-

ular structure is concerned. They all yield much residual coke, ash-free, and the effect of the process is to reduce to a marked extent the percentage of saturated hydrocarbons of which they consist and the solubility of the substance in naphtha. Without regard to the character of the petroleum in which they originate the resulting products resemble one another closely. In the table the Pittsburgh flux originated

than that of the fluxes, which are intermediate products in their preparation, except in the case of a solid residual of 1910, and in this case the oil in which it originated was probably not of as asphaltic a nature as that of previous years.

California Residual Pitches.—The California residual pitches are distinguished from those derived from Texas oil to a marked degree in that the percentage

TABLE III—ANALYSIS OF TEXAS, CALIFORNIA AND TRINIDAD RESIDUAL PITCHES

TEST No.	IDENTIFICATION	Penetration	Ductility	Bit. sol. in CS ₂	Per cent pure bit. sol. in 88° naph.	Per cent pure bit. as sat. hydrocarbons	Paraffine scale	Sulfur	Residual coke, ash-free
<i>Texas residual pitches</i>									
63,527	Texas, 1903.....	110(a)	Brittle	96.6	73.6	58.1	1.0	0.62	17.6
63,528	Texas, 1903.....	15(a)	"	95.7	66.9	48.1	1.0	0.74	21.1
68,943	Texas, 1904.....	13(a)	"	99.0	70.9	48.6	1.2	1.22	24.0
99,904	Texas, 1907.....	20(a)	"	98.3	65.2	47.8	0.5	1.06	18.5
102,529	Texas, 1910.....	18	"	98.2	70.9	65.6	0.8	..	19.5
<i>California residual pitches</i>									
126,413	Kern River oil.....	165	110	99.7	76.8	26.3	tr.	1.2	10.4
126,414	Kern River oil.....	31	130	99.6	81.9	30.0	tr.	1.3	12.9
125,485	Los Angeles refinery.....	43	130	99.5	84.0	31.1	0.6	0.82	..
127,211	S. O. Co.....	72	133	99.0	89.0	32.1	0.5	1.17	9.2
127,212	S. O. Co.....	27	18	98.9	65.3	30.7	0.2	1.38	12.9
<i>Trinidad residual pitch</i>									
125,217	Industrial scale.....	45	135	99.0	70.8	24.6	tr.	1.93	..
127,377	Run back at 400° F. in laboratory.....	50	130	99.0	77.0	30.9	tr.	2.10	..

(a) Bowen.

in Ohio paraffine petroleum, the hydrolime "B" in Texas petroleum, the Obispo in California oil, and the S. O. Co. binder in petroleum from the midcontinental field. The similarity of the effect of such treatment on all these oils is worthy of remark.

The solid residual pitches, as used for highway construction, first originated in California petroleum, but were soon followed in the Eastern market by others derived from Beaumont, Tex., oil and later in petroleum from other Texas fields. The Texas residual

of saturated hydrocarbons present is much smaller than in the case of the Texas residual pitches and the amount of residual coke, ash-free, which they yield is also smaller. They are devoid of more than a trace of paraffine scale and carry less than 1.5 per cent of sulfur, in which respect they resemble the Texas pitches.

Trinidad Residual Pitches.—Residual pitches prepared from Trinidad petroleum are differentiated from the California products by the higher percentage of sulfur, about 2 per cent, and by the smaller percentage

TABLE IV—ANALYSES OF MEXICAN RESIDUAL PITCHES

TEST No.	IDENTIFICATION	Penetration	Ductility	Bit. sol. in CS ₂	Per cent pure bit. sol. in 88° naph.	Per cent pure bit. as sat. hydrocarbons	Paraffine scale	Sulfur	Residual coke, ash-free
102,261	Ebano "E," 1908.....	42	...	99.4	60.7	31.7	1.0	5.90	19.2
102,262	Ebano "DX," 1908.....	20	...	97.9	55.0	32.4	1.3	6.33	23.9
102,263	Ebano "D," 1908.....	12	...	97.8	55.6	31.5	1.3	6.08	24.9
102,264	Ebano "B," 1908.....	5	...	95.8	47.4	32.2	1.9	6.89	30.5
126,362	"Aztec" exhibit, 1912.....	48	46	99.1	70.6	40.8	2.1	4.91	16.7
126,381	Aztec shipt., 1912.....	31	130	99.5	69.3	39.0	1.7	5.08	17.4
127,026	Montezuma.....	168	133	99.4	76.5	32.5	...	5.81	12.6
127,027	Montezuma.....	35	62	99.2	68.7	33.8	1.2	6.16	17.6
127,600	S. O. Co., March, 1913.....	36	74	99.6	71.9	41.1	2.4	5.36	15.5

TABLE V—ANALYSES OF NATIVE ASPHALTS

TEST No.	IDENTIFICATION	Penetration	Bit. sol. in CS ₂	Per cent pure bit. sol. in 88° naph.	Per cent pure bit. as sat. hydrocarbons	Sulfur	Residual coke, ash-free
63,260	Trinidad Lake.....	7	56.5	63.1	24.4	6.2	10.8
36,721	Trinidad Land.....	0	54.1	61.9	21.8	5.0	12.9
44,412	Bermudez, 1900.....	22	95.0	56.4	24.4	4.0	13.4
67,753	Bermudez, 1903.....	26	96.0	71.9	23.4	4.7	14.0
66,923	Maracaibo.....	20	96.8	47.2	25.3	5.7	18.0
22,220	Cuba, Bejucal.....	0	75.1	43.1	17.0	8.3	25.0
13,541	La Pateria, Cal.....	0	49.3	43.8	8.1	6.2	14.9

pitches are characterized by containing a small percentage of paraffine scale, less than 1.25 per cent of sulfur, and yielding, on ignition, a very high percentage of residual coke, ash-free. The amount of saturated hydrocarbons which they contain is very much smaller

of saturated hydrocarbons which they contain, lower in amount than is the case in the California residual pitches and approaching in the latter respect the solid native asphalts.

Mexican Residual Pitches.—The Mexican residual

itches are strikingly differentiated from those produced from other petroleum in that they carry from 5 to 6 per cent of sulfur, yield in the more solid forms a high percentage of residual coke, ash-free, and at the same time contain from 1 to 2 per cent or more of hard paraffine scale. The Mexican residual pitches, like the fluxes prepared from this oil, are unique as compared to others. They are also characterized by the difficulties encountered in their preparation.

In the manipulation of Mexican petroleum on an industrial scale peculiarities are immediately observed by any one familiar with the distillation of other asphaltic oils which plainly differentiate it from these, especially as represented by California and Trinidad petroleum.

Mexican petroleum may be regarded as a hybrid which, while resembling the asphaltic oils in gravity and distillates, more closely resembles the paraffine oils in its chemical characteristics and affinities. The sulfur which it contains is held very closely in combination, and it chiefly passes over with the distillates

expected. A copious agitation of steam is required during distillation in order to carry off both distillate oils and sulfur gases, and any interruption in the steam service will result in the reabsorption of sulfur gases by the residual and the production of "short" pitches.

As a further exhibit of characteristics similar to those of the paraffine oils, the Mexican petroleum has the disagreeable trait of concentrating paraffine during winter storage in the portion of its container near the bottom.

Residuum of about 400° F. flash test produced from freshly stocked crude may be expected to contain about 1.5 per cent paraffine scale, as determined by the customary method of analysis, while that produced from the ends of stock which has been exposed to winter temperature has been found to run as high as 3.5 per cent paraffine.

Preliminary operations with the Mexican petroleum in the laboratory held forth considerable promise that residuals of suitable consistency and desirable charac-

TABLE VI—ANALYSES OF GLANCE PITCHES AND SOLID NATIVE BITUMENS OTHER THAN ASPHALTS

TEST NO.	IDENTIFICATION	Penetration	Bit. sol. in CS ₂	Per cent pure bit. sol. in 88° naph.	Per cent pure bit. as sat. hydrocarbons	Paraffine scale	Sulfur	Residual coke, ash-free
<i>Glance pitch</i>								
14,145	Glance pitch, Egypt.....	0	99.7	23.6	6.5	0.0	8.5	15.0
14,143	Manjak.....	0	99.2	27.3	6.7	0.0	...	25.0
<i>Solid native bitumens other than asphalts</i>								
92,603	Gilsonite.....	0	99.0	47.7	5.9	0.0	1.7	13.0
68,940	Grahamite.....	0	94.1	0.4	0.3	0.0	1.7	53.3

as combined sulfur rather than as a gas. The Trinidad petroleum, which carries as much sulfur in the crude as the Mexican, behaves very differently in this respect, and hydrogen sulfide is evolved very copiously on distillation. The significance of this characteristic, which also applies to the California petroleum, is that the distillates from these latter petroleum may be refined for burning and other purposes at a much lower cost and are, therefore, of greater original value.

A direct comparison of the Trinidad and Mexican petroleum in this respect may be illustrated by the sulfur content of the 20° B. fuel distillates from the two oils, as follows:

	SULFUR	
	Crude Per cent	Fuel distillate Per cent
Trinidad oil.....	3.60	0.65
Mexican oil.....	3.28	2.31

Furthermore, the residual pitches produced from these two petroleum exhibit marked differences, as far as the sulfur which they contain is concerned, which is illustrated by the following data:

	PENETRA- TION	SULFUR Per cent
Trinidad residual pitch.....	50	2.10
Mexican residual pitch.....	50	5.38

The affinity of the hydrocarbons of the Mexican petroleum for sulfur necessitates the exercise of such great care in the distillation of that oil, for the production of residuals, that the uniformity of the product obtained on a commercial scale can scarcely be

teristics for use in the paving industry could be prepared from it, but it appears to be extremely difficult to obtain uniformity either in fluxing agent or asphaltic residual, and in the latter the consistency and cementitious qualities are uniquely transitory and change very materially under the methods of manipulation which are customary in the paving industry for the production of paving mixtures with heated sand or crushed stone.

It is of interest to compare the residual pitches which have been discussed with the bitumen of the native asphalts. In the latter it is found that the sulfur is always at a high figure, from 4 to 8; that paraffine scale is absent, and that the saturated hydrocarbons are reduced in amount to 25 per cent or less. It is apparent that the more asphaltic a material is the less saturated hydrocarbons it contains. It may be held that this is in part due merely to the harder consistency of the material, but Mexican residuals of the same consistency as Trinidad refined asphalt contain 8 or 9 per cent more saturated hydrocarbons than are found in the standard asphalts, Trinidad and Bermudez.

In the glance pitches, very hard and brittle materials, the saturated hydrocarbons are reduced to between 6 and 7 per cent, while in the solid native bitumens other than asphalts, such as gilsonite and grahamite, they are reduced in the former case to 6 per cent and in the latter to practically nothing.

It will be seen, therefore, that the assertion made at the beginning of this paper is justified—that petro-

leums and their products can be differentiated in the manner there described. This was suggested as long ago as 1898 in a paper published by the writer in the *Journal of the Society of Chemical Industry* for January, 1898, where data in regard to the differences in the amount of saturated hydrocarbons in various forms of bitumen were given, and the statement made that asphalts are distinguished by the large amount of sulfur they contain, the softer asphalts containing much less than the harder ones, and that it is to the presence of this material that many of the characteristics of the native bitumens are due.

The relation of sulfur to the solid native bitumens has also been commented on by Holde in his book entitled "Investigations on Mineral Oils and Fats," where he has stated:

"A bitumen would be called a native asphalt when it contains considerable amounts (2 to 10 per cent, usually over 4 per cent) of sulfur not removable by steam, when the amount of the latter in the chloroform extract which is insoluble in benzol is at least 7.5 per cent and the asphalt, separated according to the method of Marcusson and Eickman, contains 1.4 to 31 per cent of oil, with at the most 0.6 per cent of paraffine."

"A bitumen would be called a petroleum residual pitch if it contains at most 1.7 per cent of sulfur, even in the chloroform extract prepared as previously described, and further 26 to 59 per cent of oil, in which the paraffine amounted to 3.3 to 16.6 per cent."

The conclusion of Holde might well have been drawn from the data given in the writer's paper in 1898. With the knowledge which we now have in regard to the products obtained from Mexican oil and their preparation, his statements may, however, be modified and amplified at the present time.

The relation of saturated to unsaturated hydrocarbons in the native bitumens was followed up by the writer in his book, "The Modern Asphalt Pavement." In the first edition in 1905 the statement was made:

"The saturated can be separated from the unsaturated hydrocarbons by strong sulfuric acid, and this will be found to be a very important means of differentiating the oils and the solid bitumens among themselves, by determining the relative proportions of these two classes of hydrocarbons which they contain."

The relative proportion of unsaturated and saturated hydrocarbons in various bitumens has also been considered very recently by Marcusson in "Communications from the Royal Material Testing Laboratory near Berlin," Volume 30, 1912, page 77. This writer has also remarked upon the peculiar nature of the Mexican material, but as he has had no knowledge of its behavior on attempting to handle it on an industrial scale or with the industrial products as they are marketed he has not been able to draw some of the conclusions which the data available to the writer have made possible.

DISTILLATION OF TAR¹

By P. P. SHARPER

METHODS AND VALUES IN SPECIFICATIONS

The wide adoption of refined tar in road work has led to much study of the material both from a manufacturer's and a consumer's standpoint. The manufacturer is interested in the manufacture of the best possible product from the raw materials available, while the consumer is interested both in getting the best material and in holding the manufacturer up to his highest level.

Many different tests have been proposed to define refined tar, but the only essential points to be defined in order to secure uniformity are the specific gravity, viscosity or melting point, free carbon, and a distillation test. Of these tests, the specific gravity, viscosity or melting point, and free carbon have been very well understood through the discussion which has raged around them, and the tests themselves are comparatively simple, using simple apparatus.

On the other hand, with the distillation test so many variations are possible, each of them having a direct and important bearing on the result, that the standardization of a method of testing has been fraught with great difficulty. Each laboratory which has attacked the problem has chosen a form of apparatus of its own, or even where the apparatus was the same, it was used in such different ways that radically different results have been obtained with the same apparatus. It is hardly to be wondered that the manufacturer who came in contact with all these different methods had difficulties of his own in attempting to fill even a specification based on the analysis of his own material.

The sources of variation in the methods of distilling may be enumerated as follows:

1. Shape of still.
2. Size of still.
3. Position of outlet.
4. Material of still and weight.
5. Method of heating.
6. Method of protecting still and outlets from drafts.
7. Size of charge.
8. Rate of distillation.
9. Position of thermometer.
10. Accuracy of thermometer.
11. Size and shape of thermometer.
12. Cutting points on fractions.
13. Personal equation.
14. Method of reporting results (by volume or by weight).

It is not necessary to go into detail in regard to the causes of variation in the different cases enumerated, but that they are serious is shown by Tables I, II, and III. Table I shows results obtained by Messrs. Arthur R. Warnes and W. B. Southerton, of the Midland Junior Gas Association, February, 1912.

¹ Paper presented at the Cleveland meeting of the American Association for the Advancement of Science, Dec. 30, 1912-Jan. 4, 1913.

Tables II and III are taken from "Proceedings of The American Society for Testing Materials," Vol. XI, 1911, the report of the sub-committee on Distillation of Committee D-4. The three series of tests, "A," "B," and "C," were made by three different observers in three independent laboratories on the same sample, and are especially important, since they bring out not only variations due to the method, but also variations due to the personal equation.

In the case of creosote oil where a similar distillation is made, it was early recognized that every detail of the method of distillation must be clearly stated, in order that the results might have any weight. As small variations in the distillate might lead to the rejection of thousands of gallons of oil, it was important that the chemists of the buyer and of the seller should agree.

In the United States, the specification of the Maintenance of Way Association has been generally adopted for creosote oil. This specification recognized and provided for all the points enumerated above, except the size and shape of the thermometer. Some recent work on thermometers has shown that manufacturers of the instruments vary widely in their method of calibration and in the size of the different parts of the thermometer. These differences are of small account in ordinary thermometric work, but in distillation, where the range is wide and where the temperature is not stationary but advancing, it is important to define the size of the thermometer, its amount of emersion and its sensitiveness to change in temperature. If this is not done, the cutting points recorded will not be the same, since a thermometer which is lacking in sensitiveness will not arrive at the true temperature until long after that temperature has actually been reached in the distillation.

Out of the general chaos of methods proposed for road work have emerged four which are now in somewhat general use. These methods are as follows:

DISTILLATION TEST, OFFICE OF PUBLIC ROADS, WASHINGTON, D. C.

This test is made upon tars and tar products as follows: From the specific gravity of the tar, taken at 25° C., the weight of 250 cc. is calculated, and this amount poured into a tared glass retort of 750 cc. capacity. A cork stopper carrying a thermometer is then inserted into the tubulature so that the bulb is on a level with the bottom of the juncture of stem and body of the retort, as shown in Fig. 48.

The tar should be heated gradually by means of a Bunsen burner and the first fraction to 100° C. caught in a graduated glass cylinder. A cold wet towel wrapped about the stem of the retort serves to condense the distillate. If the tar is a crude one, containing much water, great care must be taken to prevent it from boiling over. After the first fraction is collected, however, distillation proceeds without trouble.

At this point the receiver is changed for another graduated glass cylinder, and an asbestos paper cover (see Fig. 49) placed over the retort for the purpose of obtaining a uniform temperature. The flame of the burner should be so regulated that not over two drops of distillate per second are collected. At 170° C. the receiver is again changed and a third fraction to 270° C. collected.

Distillation is then stopped, and any material which may have

solidified in the stem of the retort is liquefied by the application of heat and caught in the last receiver.

When the maximum temperature is reached for each fraction, the flame should be removed from under the retort until the thermometer shows a drop of about five degrees. The temperature is then changed for the next fraction.

Fig. 49. Asbestos cover for retort.

DISTILLATION TEST, AMERICAN SOCIETY OF CIVIL ENGINEERS

700 grams of the compound are weighed into a retort (E. & A. 4-pint iron retort No. 4521) whose top is fitted with a tee as close as possible to the retort, and a condenser pipe 24" to 36" long. The upper branch of the tee is used for the insertion of a thermometer, the top of whose bulb is placed immediately below the main outlet of the tee. The distillation shall proceed at the rate of two drops per second.

DISTILLATION TEST, AMERICAN RAILWAY ENGINEERING & MAINTENANCE OF WAY ASSOCIATION (Bulletin No.

65, July, 1905)

Apparatus: The apparatus for distilling the tar oil or creosote must consist of a stoppered glass retort similar to that shown in diagram, having a capacity, as nearly as can be obtained, of 8 oz. up to the bend of the neck, when the bottom of the retort and the mouth of the offtake are in the same plane.

A nitrogen filled mercury thermometer of good standard make, divided into full degrees Centigrade, must be used in connection therewith. The bulb of the retort and at least 2 inches of the neck must be and remain covered with a shield of heavy asbestos paper, shaped as shown in diagram, during the entire process of distillation, so as to prevent heat radiation, and between the bottom of the retort and the flame of the lamp or burner two sheets of wire gauze, each 20-mesh fine and at least 6 inches square, must be placed.

It is also recommended that the flame be protected against air currents. An ordinary tin can, from which a portion of the bottom and all of the top have been removed, placed on a support attached to the burner, as shown on diagram, has been found to answer the purpose.

Distillation.—Before beginning the distillation the retort should be carefully weighed, and exactly 100 grams of the oil placed therein, the same being weighed in the retort. The thermometer should be inserted in the retort with the lower end of the bulb $\frac{1}{2}$ " from the surface of the oil, and the condensing tube attached to the retort by a tight cork joint. The distance between the bulb of the thermometer and the end of the condensing tube should not be less than 20" nor more than 24", and during the progress of the distillation the thermometer must remain in the position originally placed.

The distillate should be collected in weighed bottles and all fractions determined by weight.

The distillation should be a continuous one and should take about 45 minutes.

PROPOSED TENTATIVE METHOD OF DISTILLATION OF AMERICAN SOCIETY FOR TESTING MATERIALS (Page 241, Vol. XI, 1911, "Proceedings of the American Society for Testing Materials")

Apparatus. The apparatus shall consist of the following standard parts: (a) *Flask*—the distillation flask shall be a 250 cc. Engler distilling flask, having the following dimensions: Diameter of bulb, 8.0 cm.; length of neck, 15.0 cm.; diameter of neck, 1.7 cm.; surface of material to lower side of tubulature, 11.0 cm.; length of tubulature, 15.0 cm.; diameter of tubulature, 0.9 cm.; angle of tubulature, 75°. A variation of 3 per cent. from the above measurements will be allowed.

(b) *Thermometer.*—The thermometer shall be of hardened

glass, filled with carbon dioxide under pressure and provided with an expansion chamber at the top; it shall read to 450° C., and shall be graduated in single degrees Centigrade, and shall

TABLE I—DISTILLATION OF CREOSOTE, Sp. Gr. 1.057 at 15° CENTIGRADE

	8 oz. Retort		1 lb. Retort		Per cent		Per cent	
	Ther. in liquid, bulb 3/8" from bottom of retort.	Per cent	Ther. in vapor, bulb just below neck of retort and 1" from liquid at commencement.	Per cent	Ther. bulb 3/8" from bottom of retort. Retort bulb covered with tin hood packed with asbestos.	Per cent	Ther. in vapor 1 inch above liquid. Bulb of retort covered with tin hood packed with asbestos.	Per cent
Below 140° C....	0.85	1.20	0.20	0.50	0.80	0.80	1.10	1.10
140-270° C.....	41.00	63.00	45.00	60.00	58.00	56.00	56.00	56.00
270-300° C.....	21.00	12.00	22.00	15.00	15.00	14.00	14.00	14.00
Total distillate...	62.85	76.20	67.20	75.50	73.80	71.10	71.10	71.10

TABLE II—COMPARISONS OF FRACTIONS OF SAMPLE MADE FROM WATER GAS TAR, Sp. gr. 1.1137, Free carbon 1.34

	A	B	C	A	B	C	A	B	C	A	B	C
Time, minutes.....	90	90	75	120	150	139	64	45	46	64	45	42
Per cent by weight												
Start to 110° C.....	0.00	0.20	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
110° to 170° C.....	0.23	0.85	1.44	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
170° to 235° C.....	21.50	16.21	14.61	0.80	0.60	0.00	1.63	0.40	0.35	0.07	0.08	0.37
235° to 270° C.....	20.80	8.36	24.06	10.70	6.83	4.09	10.93	4.50	4.35	11.90	11.56	7.62
270° to 315° C.....	(a)	16.22	15.73	42.80	34.30	27.59	25.50	24.00	25.67	26.97	28.66	26.41
Residue.....	57.13	58.16(b)	43.31	43.50	58.37(b)	67.35	61.80	71.10(b)	69.45	60.87	59.11(b)	65.22
Total.....	99.69	100.00	99.24	97.85	100.00	99.03	99.86	100.00	99.62	99.81	100.00	99.62

(a) Distillation carried to 270° C. only.

(b) Residue determined by difference.

TABLE III—COMPARISONS OF FRACTIONS OF SAMPLE MADE FROM COAL TAR, Sp. gr. 1.2082, Free carbon 18.53

	A	B	C	A	B	C	A	B	C	A	B	C
Time, minutes.....	96	105	84	100	210	102	93	50	35	58	50	38
Per cent by weight												
Start to 110° C.....	0.03	0.00	0.52	0.10	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
110° to 170° C.....	1.36	0.07	3.06	0.25	0.20	0.15	0.18	0.00	0.00	0.01	0.00	0.00
170° to 235° C.....	17.54	14.80	13.39	5.75	3.54	2.84	5.90	3.40	2.84	6.40	6.65	5.04
235° to 270° C.....	9.80	6.64	12.78	11.65	11.70	11.41	10.33	9.40	9.16	9.07	9.06	9.87
270° to 315° C.....	(a)	10.47	10.57	11.60	12.42	12.66	10.37	9.60	11.40	10.10	9.14	10.25
Residue.....	70.80	68.02	58.92	70.10	72.14(b)	72.00	73.07	77.60	76.45	74.10	75.15(b)	74.62
Total.....	99.42	100.00	99.24	99.45	100.00	99.06	99.85	100.00	99.85	99.69	100.00	99.78

(a) Distillation carried to 270° C. only.

(b) Residue determined by difference.

TABLE IV—COMPARISON OF REFINED TARS

	No. 5	No. 7	No. 9	No. 11
Penetration (Schütte).....	5 seconds @ 40° F.	77 seconds @ 40° F.	70 seconds @ 60° F.	M. p. 113° F.
Distillation, 0 to 170° C.....	0%	0%	0%	0%
170-315.5° C.....	26.67%	21.75%	15.99%	9.12%
Specific gr. of distillate at 15.5° C.....	1.0345	1.0433	1.0481	Not determined
Melting pt. of residue.....	72.7° C.	73.8° C.	72.2° C.	74.4° C.

have the following dimensions: Diameter of stem, 6.75 to 7.25 mm.; length of thermometer, 335 to 350 mm.; length from 0° to 450° marks, 285 to 300 mm.; length of bulb, 20 to 22 mm.; diameter of bulb, 5.25 to 6.50 mm.

It shall rise from 15° to 95° in not less than 3 seconds nor more than 5 seconds when plunged into boiling water.

The thermometer shall be set up as for the distillation test, using water, naphthalene and dimethylamine as distilling liquids. The correctness of the thermometer shall be checked at 0° C. and 100° C. after each third distillation until seasoned.

(c) *Condenser*.—The condenser shall have the following dimensions: Length of tube, 500 mm.; width of tube, 12 to 15 mm.; width of adapter end of tube, 20 to 25 mm.

(d) *Stands*.—Two iron stands shall be provided, one with a universal clamp for holding the condenser and one with a light grip arm with a cork-lined clamp for holding the flask.

(e) *Burner and Shield*.—A Bunsen burner shall be provided, with a tin shield 20 cm. long by 9 cm. in diameter. The shield shall have a small hole for observing the flame.

(f) *Cylinders*.—The cylinders used in collecting the distillate shall have a capacity of 25 cc., and shall be graduated in tenths of a cubic centimeter.

4. *Setting up the Apparatus*.—The apparatus shall be set up as shown in Fig. 1, the thermometer being placed so that the top of the bulb is opposite the middle of the tubulature. All connections should be tight.

5. *Method*.—One hundred cubic centimeters of the dehydrated material to be tested shall be placed in a tared flask and weighed. After adjusting the thermometer, shield, condenser, etc., the distillation is commenced, the rate being so regulated that 1 cc. passes over every minute. The receiver is changed as the mercury column just passes the fractionating point.

The following fractions should be reported: Start of distillation to 110° C.; 110 to 170° C.; 170 to 235° C.; 235 to 270° C.; 270 to 300° C.; residue.

To determine the amount of residue, the flask is weighed again when distillation is complete. During the distillation the condenser tube shall be warmed when necessary to prevent the deposition of any sublimate. The percentages of fractions should be reported both by weight and by volume.

The results of a long series of distillations made by members of the sub-committee on distillation, of the American Society for Testing Materials, given in Table I, show very clearly the marked difference in the results given by these methods, and also the differences that may be expected from different observers using the same methods.

If these different specifications are examined, it will be noted that the specification of the American Railway Engineering & Maintenance of Way Association provides for nearly all the possible sources of error noted on page 466. The personal equation, however, seems to enter less into the results obtained by the Tentative Method of the American Society for Testing Materials. It would seem, therefore, that this method warrants a much wider acceptance than has been accorded it at the present time. The method, in addition to its accuracy, has the distinct advantages over all the other methods (except that of the American Railway Engineering & Maintenance of

Way Association method) of requiring apparatus easily obtainable; of requiring a minimum amount of material for the distillation; and of requiring a minimum amount of time. All of these are important considerations in a commercial laboratory.

TABLE V—EXTRACTS OF VARIOUS SPECIFICATIONS

MASSACHUSETTS HIGHWAY COMMISSION'S SPECIFICATION FOR REFINED TAR, 1909: "It shall contain no body that distills at a lower temperature than 225 degrees C.; not over 10 per cent by weight shall distill below 270 degrees C.; and it shall contain at least 65 per cent, by weight, of pitch or bituminous material remaining after all bodies up to 360 degrees C. have been distilled."

ILLINOIS HIGHWAY COMMISSION'S SPECIFICATION FOR TAR BINDER, 1912: "Distillation.—Fractional distillation shall give results within the following limits, all measurements being by volume:

"Up to 110° C. the distillate shall not exceed 2 per cent, and shall be free from ammoniacal water.

"From 110° C. to 170° C. there shall be not to exceed 5 per cent distillate, of which not more than one-fourth shall be naphthalene.

"From 170° C. to 270° C. there shall be not more than 30 per cent nor less than 20 per cent of distillate, of which not more than one-third shall be solids when cold."

NEW YORK HIGHWAY COMMISSION'S SPECIFICATION FOR BITUMINOUS MATERIAL "T" (HIGH CARBON TAR), 1912: "It shall contain no body that distills at a lower temperature than 170° C.; not over 1 per cent shall distill below 235° C.; not over 10 per cent shall distill below 270° C.; not over 20 per cent shall distill below 300 degrees C.

"The specific gravity of the entire distillate shall not be less than 1.02.

"The residue from the foregoing distillation shall have a melting point not greater than 75 degrees C."

SPECIFICATIONS FOR "BITUMINOUS CONCRETE PAVEMENT," ADOPTED BY THE ASSOCIATION FOR STANDARDIZING PAVING SPECIFICATIONS IN JAN., 1912: "Coal Tar Cement.—No distillate shall be obtained lower than 338° F., and up to 600 degrees not less than 5 per cent and not more than 20 per cent of distillate shall be obtained. The distillate shall be of gravity of not less than 1.03 at 60 degrees F. The residue shall have a melting point of not more than 165 degrees F.

"In making this distillation an 8 oz. glass retort shall be used, and the thermometer suspended so that before applying the heat the bulb of the thermometer is 1/2 inch above the surface of the liquid."

ROAD BOARD OF ENGLAND'S SPECIFICATION No. 5 ADOPTED IN APRIL, 1911: "Specification for Tar No. 2.—Fractionation: The tar shall be free from water, and on distillation shall yield no distillate below 140° Centigrade, nor more than 5 per cent of distillate up to 220 degrees Centigrade, which distillate shall remain clear and free from solid matter (crystals of naphthalene, etc.) when maintained at a temperature of 30 degrees Centigrade for half an hour.

"Between 140 degrees and 300 degrees Centigrade it shall yield not less than 15 per cent, nor more than 21 per cent of the weight of the Tar."

VALUE IN SPECIFICATIONS

A distillation clause in specifications for road tar was originally introduced with the idea of governing the consistency. Methods for determining consistency have, however, been so well worked out in recent years that the distillation test is not required for this purpose, and the mistake has often been made of calling for a distillation test not in accordance with the viscosity test. The two are closely related, as is shown by Table IV, showing the total distillate of four refined road tars of differing viscosities, made from the same raw tars, as determined by the American Railway Engineering & Maintenance of Way Association method.

The real value of the distillation test is that when properly worded it defines to a certain extent the tars from which the product may be produced and the method of distilling them. The results should always be interpreted with reference to the other constants determined.

The distillation specifications may be made to show:

I. The detection of water. Water will be shown in

the first fraction and may be determined quantitatively.

II. The kind of tar. For this purpose the specific gravity of the oils distilled is indispensable and should be required. Interpreted with reference to the free carbon and the viscosity, coal tar and water gas tar may be distinguished by the specific gravity of the oils.

III. The method of manufacture. The detection of a cut back tar may be inferred from an abnormal specific gravity of oil for the viscosity, and from an abnormally high melting point of the residue of distillation. For this purpose the melting point of the residue should always be required.

IV. The presence of abnormal amounts of naphthalene. An examination of the liquefying point of the oil will indicate abnormal naphthalene.

An examination of some of the specifications in use would seem to show little uniformity in the requirements, and few indicate the method to be used, thus invalidating, to a certain extent, the objects aimed at. In Table V are shown a number of current specifications calling for approximately the same grade of refined tar. It will be noted that no two use the same cutting points, that no two specify the same end point and that only two call for the specific gravity of the distillate and the melting point of the residue.

The great variety in the specifications takes away no small part of their value, as the direct comparison of the results of different observers is prevented. The importance of the test would seem to warrant its standardization.

The important points to be observed in drawing specifications for distillation are:

1. Absolute definition of method.
2. Designation of specific gravity of oil.
3. Designation of melting point of residue.
4. Conformance of distillation specification with other parts of the specification.

297 FRANKLIN ST.
BOSTON, MASS.

THE DETERMINATION OF SULFATE IN AMMONIUM SULFATE SOLUTION WITH SPECIAL REFERENCE TO THE TESTING OF ILLUMINATING GAS¹

By R. S. MCBRIDE AND E. R. WEAVER

The following paper is a report of a short series of experiments undertaken to determine the methods most suitable for sulfate determination in the testing of illuminating gas. It is believed that some of the results obtained may be of general interest. In the use of the various forms of apparatus for determination of sulfur in gas a solution of ammonium sulfate and ammonium carbonate is obtained, and it is necessary to determine the sulfate present in such solutions. For official or commercial testing an accuracy of two or three per cent in this determination is ample; it is,

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913. This paper reports the same investigation that is given in the latter part of Technologic Paper, No. 20 of the Bureau of Standards. Published by permission of the Director, Bureau of Standards.

therefore, possible to utilize rapid methods not applicable in problems where great accuracy is needed. The methods applicable here are, in modified form, probably also suited to use on cement, iron and steel, rubber and other materials where the sulfur determination is important. In many cases where testing material supplied on contracts requires a large number of sulfate determinations, these methods may be used. In case of material very close to the limit of the specification the first quick test can be checked by more accurate but longer methods; but the larger number of samples would need test only by the short method.

The methods for sulfate determination are of three groups: gravimetric, volumetric and turbidimetric. Although most used, the gravimetric procedures are by far the slowest; in our work two modifications of this group determinations were used, both involving a weighing of barium sulfate. These two are outlined as methods 1 and 2 below, but they are of interest only to show the basis of the comparisons given later. The volumetric processes are in use very little; but for rapid and approximate work in routine testing of a large number of samples of any approximately uniform material they deserve consideration. One volumetric procedure has been used by us.

Turbidimetric methods have been little used, but experience with one such method on solutions from the various forms of apparatus to determine sulfur in illuminating gas has indicated an accuracy and speed attainable with this method such that it is promising as a generally useful analytical method.

In the following tests the only substances present in any amount in the ammonium sulfate solutions were ammonium carbonate and very small amounts of silica (dissolved by ammonia from the glass of the apparatus in which condensation took place). The four methods used are as follows:

Method 1—Gravimetric, with Evaporation to Dryness

Dilute or evaporate the sample to 300 cc., add 50 cc. of concentrated hydrochloric acid, heat to boiling, and run in 10 cc. of 10 per cent solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ through a tube or burette delivering it at the rate of 8–10 cc. per minute, stirring constantly during the addition. After evaporation to dryness on the steam bath, take up with 75–100 cc. hot water, filter, wash till the washings amount to 200 cc., ignite and weigh the barium sulfate. The precipitates thus obtained contained a trace of silica, but this could be removed easily when necessary by moistening with hydrofluoric acid and sulfuric acid, igniting and weighing again.

Method 2—Gravimetric, with Precipitation in Nearly Neutral Solution

Dilute or evaporate the sample of solution to a bulk of 300 cc., make neutral to methyl-orange¹ by adding hydrochloric acid, and add 2 cc. of the 1 : 1 acid in excess. Heat to boiling, add 10 cc. barium chloride solution as in method 1, boil 5 minutes, let stand on the steam bath a half hour or longer, filter, wash, ignite and weigh the barium sulfate as usual. The

¹ Any other indicator sensitive to ammonia but not affected by carbon dioxide, may be used.

conditions of precipitation are made uniform and the loss by solubility of barium sulfate is negligible for the present work.

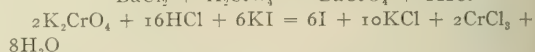
Method 3—Volumetric

This method as used by us is more like that of Holliger² than any of the others previously recommended.

Make up a solution of 50.0 g. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per liter, and one of 30.5 g. $\text{K}_2\text{Cr}_2\text{O}_7$ per liter. To 300 cc. of water add 10 cc. of 1 : 1 hydrochloric acid and exactly 15 cc. (from pipettes) of each of the above solutions; heat to boiling, add two or three drops of a dilute solution of ferric chloride, then slowly add 10 per cent ammonium hydroxide until a precipitate forms which does not redissolve on stirring. Add 5 cc. of the ammonia solution in excess, boil 5 minutes, filter and wash thoroughly with hot water. Allow the filtrate to cool, acidify with hydrochloric acid, add two grams of solid potassium iodide or a solution containing that amount, and titrate with tenth-normal sodium thiosulfate, using starch as an indicator. The amount of thiosulfate solution used in this blank is to be subtracted from the amount used in each subsequent determination.

To make a determination of the sulfate in a solution, dilute or concentrate the sample taken to 300 cc.; add 10 cc. of 1 : 1 hydrochloric acid; heat to boiling; add 15 cc. of barium chloride solution from the pipette used in the blank test; boil five minutes; add 15 cc. of potassium bichromate solution and a few drops of ferric chloride, precipitate with ammonium hydroxide and complete the determination exactly as in the blank test. From the amount of thiosulfate solution used subtract the amount required in the blank. The remainder represents the sulfate in the sample taken.

The reactions upon which the method is based are:



From the above equations it will be seen that three $\text{Na}_2\text{S}_2\text{O}_3$ are equivalent to one S, hence 1 cc. N/10 $\text{Na}_2\text{S}_2\text{O}_3$ solution is equivalent to 1.069 mg. (0.0165 grains) of sulfur.

The above method was selected in preference to other methods previously used, which have been open to the following objections:

1. In those using a hydrochloric acid solution of barium chromate the reducing action of the acid on the chromate has introduced serious errors.³

2. In those which use exactly equivalent amounts of barium chloride and potassium chromate it is somewhat difficult to make the solutions of exactly the right strength and a blank test must be made.³

3. The use of a suspension of barium chromate or of

¹ Z. anal. Chem., **49**, 84 (1910).

² Andrews, Am. Chem. J., **11**, 567 (1889); Pennock, J. Am. Chem. Soc., **26**, 1265 (1903); Holliger, Z. anal. Chem., **49**, 84 (1910); Bradley, Chem. Eng., **13**, 26 (1911); Reuter, Chem.-Ztg., 357 (1898).

³ Roemer, Z. anal. Chem., **49**, 490 (1910); Precht, Z. anal. Chem., **18**, 521 (1879).

the solid is less convenient than that of solutions and as it is sometimes difficult to obtain the barium salt free from alkali chromate, a blank test should also be made with this method.¹

4. In all methods the solubility of the barium chromate should be taken into account.

All of these sources of error or difficulty are taken care of by a single blank test when the chromate solution is slightly stronger than the barium chloride solution, as in the method described. The solubility of barium chromate is somewhat affected by the concentration of ammonium chloride and of ammonium hydroxide in the solution;

but by having the same bulk of solution, adding the same amount of hydrochloric acid and precipitating in the same manner in the blank as in the

ide, as recommended by Holliger,² aids greatly in collecting the precipitate of BaCrO_4 and BaSO_4 for the filtration.

Method 4 Turbidimetric³

The turbidimeter used (shown in Fig. 1) consists of a cylindrical glass tube graduated from the bottom in centimeters, surrounded and held in place above the light by a brass tube. The light used in most cases was a 16 candle power carbon filament lamp, so placed that a straight portion of the filament extended diametrically across just below the bottom of the tube.

The following method was adopted after tests, the results of which are given later in this paper; it is recommended for general use when a turbidimetric procedure is wanted. The directions are given for use in connection with an apparatus for sulfur in gas, but can easily be applied to solutions otherwise obtained.

The condensate and washings from the sulfur apparatus are neutralized with hydrochloric acid,³ then 2 cc. of the 1 : 1 acid added in excess. The solution is measured (to the nearest cubic centimeter) and a 90 cc. portion placed in a small beaker for the test.

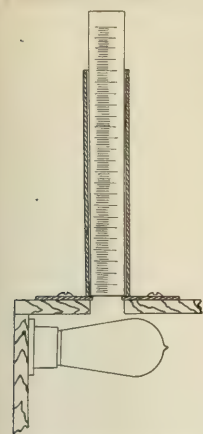


FIG. 1 TURBIDIMETER

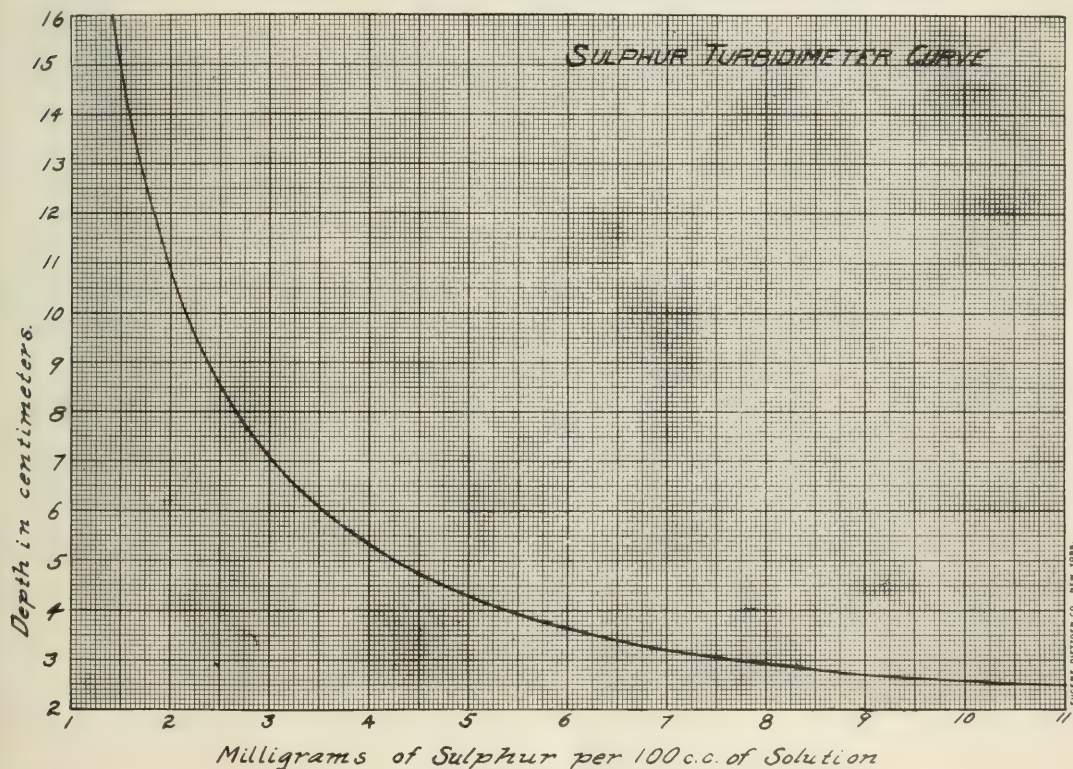


FIG. 2

determination, the effect of this source of error is also eliminated. The use of a small amount of ferric chlor-

It may be measured in an ordinary graduated cylinder

¹ *Loc. cit.*

² Hinds, *J. Am. Chem. Soc.*, **18**, 661 (1896); **22**, 269 (1900); **24**, 848 (1902).

³ An indicator is required which is sensitive to ammonia but not to carbon dioxide. Para nitrophenol is the most satisfactory because it is colorless in acid solution.

¹ Bruhns, *Z. anal. Chem.*, **45**, 573 (1906); Kowarowsky, *Chem. Ztg.*, **498** (1907).

if it is certain that the ratio of the small cylinder to the larger measuring vessel first used, is correct. While the solution is between 25 and 30° C., 10 cc. of a 10 per

(Fig. 2) corresponding to the depth of a liquid in the turbidimeter measurement is multiplied by the number of cc. of neutralized condensate and

divided by 90 (the cc. of sample taken) to give the total amount of sulfur obtained by burning the gas. For convenience in this calculation the condensate after neutralization can be made up to 270 or 360 cc. and the observed values for the 90 cc. portion are then multiplied by 3 or 4.

The curve of Fig. 2 may be used by any observer if care is exercised in following exactly the method given in the preceding paragraph; the acidity and temperature limits must be particularly observed; the character of light used is less important. In any case it is well for an inexperienced observer to take known amounts of a standard sulfuric acid solution and run through the test until assured that his observations are con-

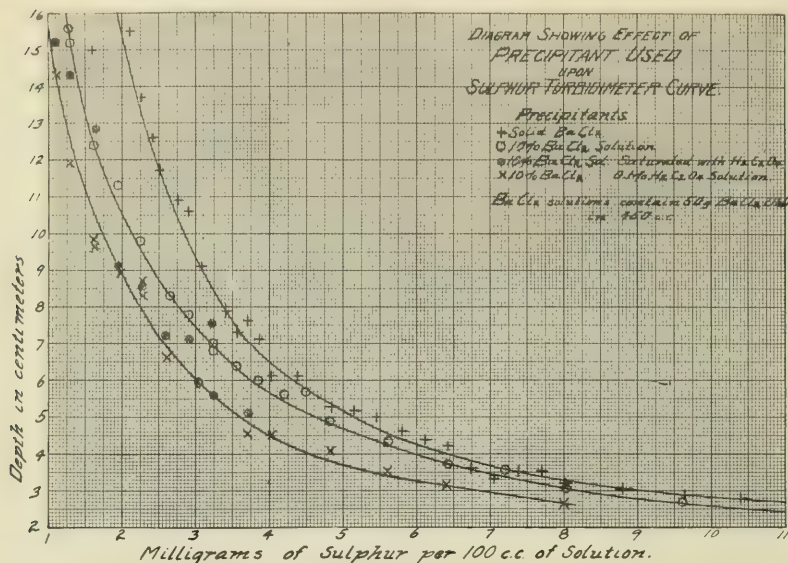


Fig. 3

cent solution of $BaCl_2 \cdot 2H_2O$ is added and the whole stirred vigorously until the precipitation appears to be complete. (This usually requires less than one minute's stirring).

The suspension is now poured into the clean and dry turbidimeter tube, a small portion at a time, until the filament of the lighted lamp disappears from view. After the first trial the solution is poured back into the beaker, stirred vigorously and the observation of the point at which the filament disappears is repeated until this is fixed within one millimeter. During the time the solution is being added the portion remaining in the beaker should be kept well stirred so that the small portions added from it will be representative of the whole bulk. The first time the solution is poured into the observation tube the latter must be dry and clean; in cleaning it care should be taken to remove, without scratching the tube, the film of sulfate which adheres so persistently to the bottom.

Further tests on a second and 90 cc. of the original neutralized solution of sulfate should be made, if considerable accuracy is needed. The amount of sulfur indicated by the curve

sistent and correct.

Since little was known of the effect of different conditions of operation on the result of the tests, a number of special comparisons were made, the results of which are given in the following paragraphs.

The incandescent filament gives a sharper end point

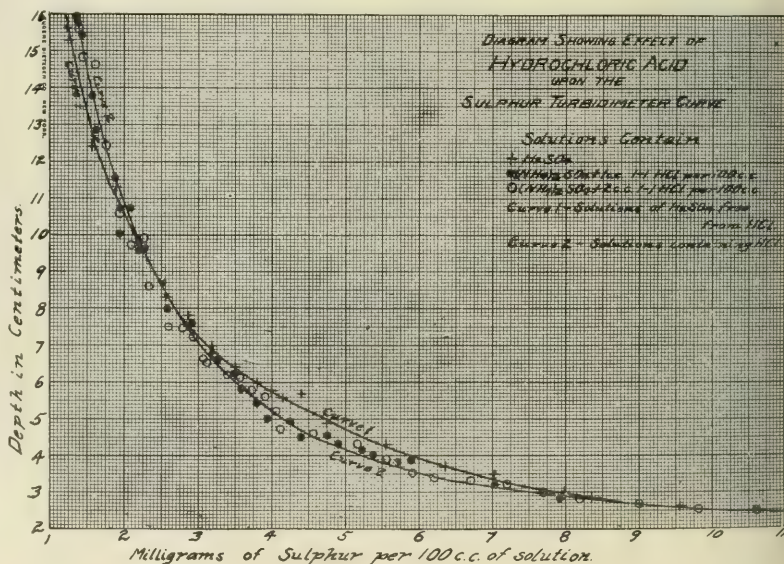


Fig. 4

than any other source of light so far devised;¹ it is

¹ See Jackson, J. Am. Chem. Soc., **23**, 799 (1901); Parr, THIS JOURNAL, **1**, 689 (1909); Leighton, U. S. Geological Survey, Water Supply and Irrigation, Paper **161**, 27 (1905).

not affected by draughts, does not smoke nor crack the tube, and can be conveniently placed under a table or in any other out of the way place. A series of comparisons using the incandescent filament, the standard candle and the 0.5 mm. slot recommended by Leighton¹ is given in Table I. In each case the same liquid was used with each source of light in turn. It can be seen that the three light sources give excellently agreeing results.

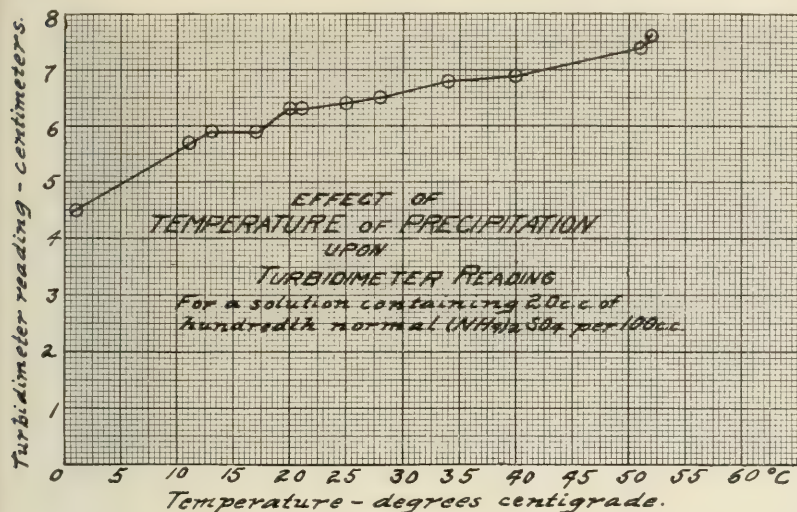


Fig. 5.

The effect of using different precipitants as proposed by various persons using the turbidimeter for sulfate determinations, is shown in Fig. 3. It will be observed that there is less variation where 10 per cent $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ solution is used than with other precipitants;

TABLE I—COMPARISON OF RESULTS WITH DIFFERENT LIGHTS IN TURBIDIMETER

Incandescent filament		Candle		Electric light below a 0.5 mm. slot	
Depth of solution	Milligrams of sulfur	Depth of solution	Milligrams of sulfur	Depth of solution	Milligrams of sulfur
24.0	1.13	25.0	1.12	25.0	1.12
20.3	1.22	20.6	1.21	20.4	1.22
12.3	1.77	12.3	1.77	12.2	1.79
11.6	1.86	11.8	1.85	11.6	1.86
8.5	2.48	8.5	2.48	8.4	2.51
7.2	2.93	7.0	3.01	7.2	2.93
5.9	3.60	6.1	3.50	5.9	3.60
5.4	3.95	5.4	3.95	5.2	4.09
4.1	5.25	4.1	5.25	3.9	5.55
3.7	5.93	3.8	5.77	3.7	5.93
3.4	6.50	3.5	6.26	3.3	6.70

the addition of oxalic acid gave a finer precipitate and a sharper end point, but successive determinations were more discordant. Agreement of duplicates and certainty of result is most desirable in this method, since in any case the results are fixed by comparison with results on known amounts of sulfur. Variation of a single test from the average of all is therefore serious, but the shape of the calibration curves is not of influence, so long as regular and calibration tests are made in the same way.

¹ Loc. cit.

Fig. 4 shows the effect of small amounts of hydrochloric acid upon the turbidimeter curve. Larger amounts caused much greater variations. Fig. 5 shows the effect of temperature of precipitation upon solutions of average strength. Fig. 2 is the curve drawn from the results obtained under the conditions of precipitation recommended above.

To show the accuracy of the method as used, the tests of one series from which our conclusions are drawn have been summarized in Tables II and III. This summary shows the average and the maximum deviation of individual tests from the value calculated from the amount of standard sulfuric acid used, i. e., the errors which were found by making a single precipitation of barium sulfate and suitable observations on it. When more than one portion is precipitated and used for a determination the accuracy would be materially increased, so that in tests on three portions of a solution the average of the three ought not to be more than one per cent in error. It should be remembered that three tests can be made in this way much more quickly than a single test by any other method.

TABLE II

Sulfur (mg. per 100 cc.)	Average error (per cent)	Maximum error (per cent)	No. of determinations
1-2	2.9	8.7	13
2-3	3.5	7.1	13
3-4	2.5	7.7	17
4-5	2.6	6.3	8
5-6	1.3	5.2	7
6-8	2.6	5.6	7
8-11	3.4	6.3	5
All values	2.7	8.7	70

From its very nature, as a procedure using a standard of similar nature as basis of calibration, the turbidimetric method must give, on the average, correct results; the variation of individual results from the

TABLE III—SHOWING PERCENTAGE OF ERROR OF DETERMINATIONS BETWEEN 2 AND 8 MG. PER 100 CC.

Error (per cent)	Number of determinations
0.0-0.5	11
0.5-1.5	12
1.5-2.5	5
2.5-3.5	7
3.5-4.5	3
4.5-5.5	5
5.5-6.5	6
6.5-7.5	2
7.7	1
	52

average is, therefore, the important consideration. The data of Tables II and III show that when used with only ordinary care it is applicable to work where approximate values (to 4 or 5 per cent of the amount

of sulfur present) are sufficient. To give an idea of the results to be had by the other three methods, Table IV has been included. These data show the results which were obtained under conditions distinctly unfavorable for accurate results, only 6 to 30 mg. of sulfur and large and varying amounts of ammonium carbonate being present in the samples used. These conditions were chosen as representing those with which we had to deal in the gas testing; and if in other work larger amounts of sulfur were present or greater care was exercised no doubt much more exact results could be had. For gas testing the accuracy here shown is ample, since it is greater than the accuracy obtainable in the condensation of the sulfate.

TABLE IV.—COMPARISON OF METHODS FOR SULFATE DETERMINATION. SULFUR (MG. PER G. OF SOLUTION) IN STANDARD H_2SO_4 SOLUTION DETERMINED BY DIFFERENT METHODS IN PRESENCE OF EXCESS OF AMMONIUM CARBONATE EXCEPT AS OTHERWISE NOTED

Volumetric against NaOH and benzoic acid	Method 1 Gravimetric	Method 2 Gravimetric	Method 3. Volumetric	
			Oxalate standard (no carbonate added)	H_2SO_4 standard
1.589	1.591	1.597	1.602	1.595
93	91	93	1.597	1.602
90	90	92	1.600	1.597
92	1.609(a)	99	1.599	1.601
92	1.596	97	1.602	1.596
92	96	92	—	1.589
89	88	99	—	1.574
90	92	91	—	1.575
—	94	1.600	—	—
Av. 1.591	1.592	1.595	1.600	1.589

(a) Omitted from average.

The first set of results in Table IV by Method 3 are calculated on the basis of the value of the thiosulfate solution obtained by titration against a permanganate solution, whose value was obtained against sodium oxalate. In the second series the thiosulfate was standardized against the sulfuric acid value given in the first column of the table.

For accurate work the gravimetric methods, with the precautions which have been carefully developed by many experimenters, are to be preferred; but for rapid work the turbidimetric and volumetric methods are very useful. They can be applied in many lines of work other than gas testing, since in each the value of the standard is fixed against similar material whose value has been previously established by other methods. If the calibration and testing procedures are identical the variation of individual tests from the average or correct value is the important factor; this variation has been shown by our experience to be about one per cent or less in the volumetric and five per cent or less in the turbidimetric method.

BUREAU OF STANDARDS
WASHINGTON

THE DETERMINATION OF SULFUR IN ILLUMINATING GAS¹

By R. S. McBRIDE AND E. R. WEAVER

The methods for determination of sulfur in gaseous

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913. Published by permission of the Director of the Bureau of Standards. This paper is a report on tests made at this Bureau, preparatory to the recommendation of a method for official inspection of gas; a more complete report on this same investigation is to appear soon in Technologic Paper No. 20 of the Bureau.

fuels can be classified in four groups, the general principles of which are as follows:

(1) The gas is burned and the sulfur oxides in the products of combustion are condensed or absorbed, oxidized to sulfate, and determined as such.

(2) The sulfur compounds are oxidized by liquid reagents giving the sulfate, which can be determined directly.

(3) The sulfur compounds are oxidized by burning the gas but the sulfur is absorbed and determined as sulfur dioxide.

(4) The sulfur compounds are reduced to give hydrogen sulfide, which is then absorbed and determined.

The methods of Group 1 have been most used in American practice and are generally considered the most accurate and convenient, either for works control or official testing. Tests have been made on five forms of apparatus of this group and one or more forms of each of the other classes; but the principal investigation was limited to the three forms, all of group one, which appeared to be most satisfactory for general use. These are known, respectively as the Referees apparatus, the Hinman-Jenkins apparatus, and the Elliott apparatus.

The Referees apparatus is too well known to require a detailed description here. It consists of a Bunsen burner surrounded by pieces of crystallized ammonium carbonate, from which the products of combustion of the gas, mingled with vaporized ammonium carbonate, pass into a condensing cylinder where the sulfur oxides are absorbed in the water condensed from the products of combustion and are oxidized, in the presence of the ammonia, to ammonium sulfate.

The Elliott apparatus is essentially a large Referees apparatus, the principal difference being the use of two condensing cylinders through which the gases successively pass. The Hinman-Jenkins apparatus¹ differs from the Referees greatly in form, but in principle only in the use of concentrated ammonium hydroxide instead of ammonium carbonate as a source of ammonia.

To compare the several forms of apparatus, two or more were operated at the same time, being supplied with gas from a common source. Suitable precautions to maintain a uniform supply to each apparatus and to prevent errors due to sulfur in the air of the room were taken. The meters used were frequently compared to determine their relative accuracy.

One series of comparisons made upon the three apparatus to determine the best conditions of operation and sources of error is summarized in Table I. The results tabulated include only those obtained under normal working conditions, and not those obtained when variations were made which would be avoided in practice. The sulfate in the condensed liquids was determined as barium sulfate by a method closely resembling that of Johnston and Adams,² the weight

¹ J. Am. Chem. Soc., **28**, 543 (1906).

² *Ibid.*, **33**, 829-45 (1911).

of the precipitate being corrected for silica dissolved from the glass by the alkaline liquids.

The cause of the lower results obtained by the use

TABLE I—FINAL COMPARISON OF REFEREES, ELLIOTT AND HINMAN-JENKINS APPARATUS

A. Gas burned at the rate of: Referees 0.60, Elliott 0.96, Hinman-Jenkins 0.60 cu. ft. per hour.

Test No.	Refer-ees No. 1:		Ratio Elliott:		Ratio Hin.-Jenk.:		Ratio Hin.-Jenk.:	
	Sulfur	per 100 cu. ft.	per 100 cu. ft.	per 100 cu. ft.	Sulfur	per 100 cu. ft.	Sulfur	per 100 cu. ft.
10	11.3	10.9	98.2
11	13.8	14.3	103.6	13.8	100.0	103.7
12	13.9	14.8	106.6	14.7	106.0	100.8
13	13.4	13.9	104.1	13.7	103.3	101.3
14	13.4	12.6	93.8	14.0	104.7	90.0
15	13.5	14.8	109.9	14.0	103.7	106.0
16	13.8	14.0	101.0
17	13.6	13.8	101.5
Av.	102.7	...	102.9	100.3

B. Gas burned at the rate of: Referees 0.49, Elliott 1.20, Hinman-Jenkins 0.65 cu. ft. per hour.

Test No.	Refer-ees No. 1:		Ratio Elliott:		Ratio Hin.-Jenk.:		Ratio Hin.-Jenk.:	
	Sulfur	per 100 cu. ft.	per 100 cu. ft.	per 100 cu. ft.	Sulfur	per 100 cu. ft.	Sulfur	per 100 cu. ft.
18	15.2	14.9	98.0	14.3	94.0	104.1
19	13.9	14.0	101.0	13.0	93.6	107.8
20	14.3	13.3	93.0
21	15.4	14.4	93.5
22	13.1	13.1	100.0	12.9	98.5	101.7
23	13.2	12.2	92.5
Av.	99.7	...	94.2	104.4

C. Gas burned at the rate of: Referees 0.50, Elliott 1.20, Hinman-Jenkins 0.50 cu. ft. per hour.

Test No.	Refer-ees No. 1:		Ratio Elliott:		Ratio Hin.-Jenk.:		Ratio Hin.-Jenk.:	
	Sulfur	per 100 cu. ft.	per 100 cu. ft.	per 100 cu. ft.	Sulfur	per 100 cu. ft.	Sulfur	per 100 cu. ft.
24	13.8	15.0	108.5	13.9	100.7	107.9
25	10.3	9.9	96.0	9.9	96.0	100.0
26	16.1	16.6	103.0
27	13.5	13.9	102.6
28	11.6	12.1	103.9
29	13.2	13.0	98.3
Av.	102.5	...	100.3	103.9

of the Referees apparatus was next investigated. It was found that by the addition to the Referees apparatus of a second condenser, which practically doubled its condensing surface, the amount of sulfur found was increased by about 1 per cent.

The effect of varying the rate at which the gas was burned, shown in Table I, is still better indicated in Table II, which shows the percentage of sulfur condensed in each tower of the Elliott apparatus with the gas burning at three different rates. The significance of the results appears at once when we remember that the first tower with its connections is practically a large Referees apparatus and the sulfur which passes into the second tower is lost in the Referees form.

From our experiments we believe that for each apparatus there is a certain rate of gas consumption above which the loss of sulfur increases out of all proportion to the increased rate at which the gas is burned. If the ammonium carbonate or hydroxide is renewed as frequently as is recommended, one cubic foot per hour for the Elliott and one-half cubic foot per hour for the other forms of apparatus are safe rates; but the loss increases rapidly at higher rates. Indeed, the amount of sulfur condensed per hour in the Elliott apparatus was less when the gas was burning at 1.36 cu. ft. per hour than when burning at 1.20 cu. ft. per hour.

Our work throughout indicated that the most

TABLE II—AMOUNT OF SULFUR CONDENSED IN DIFFERENT PARTS OF THE ELLIOTT APPARATUS AT DIFFERENT RATES OF GAS CONSUMPTION

Rate (cu. ft. per hr.)	Sulfur in 1st tower (grains per 100 cu. ft. of gas)	Sulfur in 2nd tower (grains per 100 cu. ft. of gas)	Total sulfur (grains per 100 cu. ft. of gas)	Referees burned at 0.5 cu. ft. per hr. condensed (sulfur, grains 100 cu. ft. of gas)	
				Per cent of total	at 0.5 cu. ft. per hr. condensed (sulfur, grains 100 cu. ft. of gas)
1.36	5.7	3.7	9.4	39	15.5
...	8.2	4.7	12.9	36	14.2
...	4.9	1.5	6.4	23	11.5
1.20	13.9	1.1	15.0	8	13.8
...	9.4	0.5	9.9	6	10.3
...	14.8	1.8	16.6	8	16.1
0.9	11.5	1.7	13.2	1	13.7
...	10.4	3.9	14.3	3	12.8
...	10.7	2.5	13.2	2	12.4
...	12.1	1.6	13.7	1	13.6
...	12.2	2.0	14.2	1	13.8
...	13.1	2.1	15.2	1	15.0

serious source of error in any apparatus of this type is an insufficient or irregular ammonia supply.

Table III shows the effect of using in the Referees apparatus lumps of carbonate which had previously been used and which were, therefore, incrustated with bicarbonate. As much ammonium carbonate was used in each case as would lie in the annular space about the burner. From the decrease in efficiency of condensation on long use of the carbonate, shown by the results in Table III, it appears that a 10-hour run, using a single supply of carbonate, could hardly be expected to give more than 90-95 per cent or a 20-hour run more than 75-80 per cent of the sulfur burned.

TABLE III—EFFECT OF USING OLD AMMONIUM CARBONATE ON REFEREES APPARATUS

Test No.	Previous use of carbonate (hours)	Length of run (hours)	Sulfur condensed with fresh old carbonate (grains)		Ratio of A to B
			A	B	
30	6.0	6.5	7.0	14.0	0.50
31	6.0	6.5	11.5	14.9	0.77
32	6.5	6.0	9.5	13.9	0.78
33	6.0	6.0	11.0	13.6	0.81
34	No carbonate used		5.1	16.8	0.30

Table IV shows the effect of varying the ammonia supply to the Elliott apparatus upon the percentage of the total sulfur which escapes from the first tower and is collected in the second. Similarly, Table V shows the percentage of total sulfur collected in the added condenser of the Referees apparatus previously mentioned under Table I: *first*, when nothing was added to this second condenser; *second*, when concentrated ammonium hydroxide was slowly dropped in at the top of the second condenser; *third*, when a solution of hydrogen peroxide and ammonium hydroxide was added in the same way. The object of adding hydrogen peroxide was to see what effect an oxidizing substance would have upon the absorption of the sulfur dioxide; from the results obtained this effect appears to be negligible.

Another series of experiments showed that alkalinity of the atmosphere as distinguished from alkalinity of the condenser surface was necessary for proper condensation of the sulfur.

SUMMARY

A comparison of the Referees, Hinman-Jenkins, and

Elliott apparatus for the determination of sulfur in gas showed that any of these apparatus is capable of giving satisfactory results if properly operated.

TABLE IV—PERCENTAGE OF TOTAL SULFUR CONDENSED IN SECOND TOWER OF ELLIOTT APPARATUS BURNING 1.2 CU. FT. OF GAS PER HOUR

(NH ₄) ₂ CO ₃ renewed every three hours	(NH ₄) ₂ CO ₃ renewed every hour	Air supplied to apparatus bubbled through conc. NH ₄ OH
7.5	0.6	0.1
6.0	0.8	...
8.0

TABLE V—PERCENTAGE OF TOTAL SULFUR CONDENSED IN ADDED CONDENSER OF REFEREE'S APPARATUS

Nothing added to second condenser	NH ₄ OH added to second condenser	NH ₄ OH + H ₂ O ₂ added to second condenser
1.0	3.6	1.2
1.1	2.2	2.3
0.8	0.9	2.0
...	...	1.0
Average	1.0	2.2
		1.6

Three important conditions for successful operation are: (1) A proper rate of combustion; (2) a strongly alkaline atmosphere in the condenser chamber; and (3) elimination of all rubber connections between the burner and condenser.

BUREAU OF STANDARDS
WASHINGTON

SOME RESULTS OF THE HYPOCHLORITE DISINFECTION OF THE BALTIMORE CITY WATER SUPPLY¹

By J. BOSLEY THOMAS AND EDGAR A. SANDMAN

Stokes and Hachtel² have reported the results obtained by the hypochlorite disinfection of the Baltimore City water supply during a period extending from the institution of the treatment on June 15, 1911, to October 30, 1911. They examined samples taken from the untreated water in the impounding reservoir and from the treated water after it had passed through each of two storage reservoirs. The results of their examinations showed bacterial reductions varying between 94.5 and 99 per cent. They also showed average reductions in the *Colon bacillus* from 57.5 per cent positive tests with 0.1 cc. of untreated water to 12 per cent positive tests with 0.1 cc. of treated water, and from 89 to 40 per cent with 1.0 cc. The greatest reductions were obtained with one part per million of available chlorin, when there were shown reductions from 86 per cent positive tests with 0.1 cc. of untreated water to 9.5 per cent positive tests with 0.1 cc. of treated water, and from 100 per cent to 37 per cent with 1.0 cc.

The period covered by the following report extends from January to December, 1912. In addition to the places sampled by Stokes and Hachtel, we obtained samples at the influent of the first storage reservoir, after the water had passed through seven miles of tunnel subsequent to treatment. The time required for the water to pass through this tunnel varies between 4.9 and 12.2 hours. While allowing sufficient time for effective disinfection, the taking

of samples just before the water enters the first storage reservoir permits of counts being obtained before any after-growths are likely to have occurred.

The amount of available chlorin applied during the period covered by the report of Stokes and Hachtel was raised from 0.4 part per million, applied at the start on June 15, to 0.6 on June 23, and to 1.0 on October 15. On July 15, 1912, the amount was again raised, by order of the Commissioner of Health, to 1.5 parts per million, and this amount has been maintained until the present time.

From June 11 to November 12, 1912, aluminum sulfate, in amounts varying between 0.61 and 1.05 grains per gallon, was applied to the water as it entered the first storage reservoir.

Shortly after the period covered by the report of Stokes and Hachtel, after-growths in the storage reservoir caused excessive bacterial counts. These conditions maintained during the first five months of the year, but about the middle of May the counts showed a marked diminution, and no further after-growths were observed, excepting during a few days in September.

The monthly averages of the results in bacterial counts and *B. coli* tests, shown in an accompanying table, are taken from daily analyses. The counts during the first six months were obtained on standard agar at 20° C., and during the remainder of the year at 37° C. The *B. coli* averages were obtained from tests made on portions of water varying by a multiple of ten from 0.001 cc. to 100 cc., sufficient number of tubes being used in each case to secure at least one negative and one positive test, excepting when no fermentation was obtained with 100 cc. The average number of *B. coli* per cc. for each month was estimated by considering the number of positive and negative tests in each dilution and following the method described by Phelps before the American Public Health Association in 1907. Lactose bile was used as an initial medium, and Endo's agar was used for isolating the members of the *B. coli* group in pure culture, nearly 100 per cent successful isolations having been obtained by the use of this medium, whereas the frequent encountering of spreaders on litmus agar and the fact that many of the acid-forming colonies proved not to be members of the *Colon* group seriously impaired the efficiency of this latter medium. No attempt was made until in the last two or three months to differentiate the four members of the *Colon* group; but this is now being done with the use of dulcitol, in addition to the usual sugars, and morphological examinations, and the results seem to show a greater vulnerability of the two *B. coli* organisms than of *B. aerogenes* and *B. acidi lactici*.

The results obtained by the use of the 20° temperature show much greater reductions in the bacterial count than those obtained with the 37° temperature, and we believe that counts should be made at the higher temperature in addition to those made at 20°.

The effects of the treatment of this water supply have been a very good reduction in the bacterial count of the water as it enters the first storage reservoir,

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913.

² *Am. J. Pub. Health*, April, 1912.

MONTHLY AVERAGES OF BACTERIAL COUNTS AND B. COLI TESTS IN THE BALTIMORE CITY WATER SUPPLY BEFORE AND AFTER TREATMENT

Month	Grains per gallon Coagulate added	Parts per million available Chloride	Impounding reservoir effluent before addition of hypochlorite				Tunnel effluent 4.9-12.2 hrs. after treatment				First storage reservoir effluent 5-15 days after treatment		Second storage reservoir effluent 8-25 days after treatment	
			Bacteria per cc. 20° C.		B. Coli per cc.		Bacteria per cc. 20° C.		Per cent reduction		Bacteria per cc. 20° C.		B. Coli per cc.	
Jan.	0.000	1.00	1,100	1.70	43	95.91	0.0012	99.99	42,000	0.0012	28,000	0.016	26,000	0.0037
Feb.	0.000	1.00	1,600	2.56	8	99.51	0.0022	99.99	42,000	0.0023	55,000	0.0100	55,000	0.0100
Mar.	0.000	1.00	14,000	7.21	116	99.17	0.0000	100.00	19,000	0.012	85,000	0.0120	85,000	0.0120
April	0.000	1.00	1,800	31.4	10	99.46	0.0000	100.00	80,000	0.036	80,000	0.0400	80,000	0.0400
May	0.000	1.00	9,500	27.1	12	99.88	0.094	99.66	19,000	0.062	7,000	0.0790	7,000	0.0790
June	0.952	1.00	2,400	39.0	81	96.61	0.33	99.16	100	0.120	525	0.120	525	0.120
Average			5,100	13.16	45	99.11	0.0712	99.46	31,428	0.0414	41,917	0.0441	41,917	0.0441
<hr/>														
July	1.05	1.25	4,200	2.80	42	99.01	0.0000	100.00	27	0.0020	180	0.0070	180	0.0070
Aug.	0.846	1.50	550	40.0	23	95.71	0.0020	99.99	36	0.019	210	0.0300	210	0.0300
Sept.	0.867	1.50	450	42.6	67	85.08	0.0030	99.99	300	0.251	225	0.178	225	0.178
Oct.	0.506	1.50	240	26.0	31	87.25	0.0025	99.99	48	0.300	55	0.300	55	0.300
Nov.	0.610	1.50	875	24.2	33	96.22	0.095	99.61	24	0.083	26	0.096	26	0.096
Dec.	0.000	1.50	325	7.81	36	88.58	0.064	99.20	35	0.0014	30	0.0010	30	0.0010
Average			1,100	23.9	38	91.97	0.0277	99.79	79	0.109	120	0.102	120	0.102

TYPHOID FEVER IN BALTIMORE, JAN., 1906, TO DEC., 1912, SHOWING DECREASE IN MORBIDITY AND MORTALITY SINCE THE USE OF HYPOCHLORITE

Month	1906		1907		1908		1909		1910		Average 1906-1910		1911		1912	
	Case incidence	Deaths	Case incidence	Deaths	Case incidence	Deaths	Case incidence	Deaths	Case incidence	Deaths	Case incidence	Deaths	Case incidence	Deaths	Case incidence	Deaths
Jan.	31	12	43	12	47	7	39	16	40	7	40	7	55	11	47	9
Feb.	31	6	16	5	26	9	23	3	25	11	24	11	31	3	28	7
Mar.	25	6	37	6	36	3	20	5	30	12	29	6	35	5	33	11
April	67	11	35	17	24	2	22	4	22	4	36	11	44	8	37	10
May	143	12	65	3	40	3	23	5	31	2	60	5	56	7	30	3
June	87	5	41	6	47	3	41	6	46	8	52	4	34	8	57	3
July	105	14	78	22	149	24	107	11	110	7	110	16	89	4	98	15
Aug.	284	34	217	23	339	35	217	20	473	30	306	28	280	22	198	22
Sept.	206	32	469	41	364	29	312	24	398	49	349	35	241	31	212	18
Oct.	125	26	241	47	187	30	138	23	359	42	210	34	170	28	190	12
Nov.	59	15	87	31	99	25	61	10	251	37	111	24	104	19	77	9
Dec.	46	10	91	7	68	10	66	9	106	26	75	14	62	8	76	17
	1209	183	1420	230	1426	180	1069	136	1891	235	1403	193	1201	154	1083	136

and almost entire elimination of the members of the *B. coli* group, the treated water during three months showing none of these organisms at any time in 100 cc.

The reduction in the number of cases of typhoid fever occurring in Baltimore during 1912 is 31 per cent, compared with an average of the number of cases occurring during the years from 1906 to 1910, and 24 per cent, compared with the number of cases occurring during 1911, in the last six months of which the water supply was treated.

We wish to acknowledge indebtedness to Mr. Ezra B. Whitman, Water Engineer, and to Mr. Emory Sudler, Engineer in charge of the improvement of the water supply, for an interest unusual with engineers not directly acquainted with the details of the laboratory work.

WATER DEPARTMENT
CITY OF BALTIMORE

WILD LETTUCE RUBBER¹

By CHARLES P. FOX

We have in the Central United States, two representatives of the *Compositae* which might be regarded

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913.

as possible rubber producers. These are members of the genus *Lactuca* (Wild Lettuce), one of these species, *L. Canadensis*, being a native while the other, *L. Scariola*, is of European origin. Both are widely distributed and in some sections are very abundant and often regarded as troublesome weeds.

Lactuca Canadensis.—A native biennial plant found growing everywhere across the continent from Oregon to the Carolinas. A vigorous, robust plant, three to twelve feet high; stems stout, hollow, purple; leaves large, irregularly cut and toothed, dull green; flowers small, numerous, yellow to white; seeds small with usual cottony appendages which aid in its distribution; odor strong, acrid. All portions of the plant, especially the stem, secrete, when bruised, an abundance of thick latex which rapidly coagulates to a yellowish semi-solid. Found in damp situations, growing upon rich soil, especially on newly cleared lands. Known as "Fireweed," "Trumpetweed."

Lactuca Scariola.—A naturalized annual from Europe. Stem three to four feet high, erect, branching, armed with stiff, sharp spines; leaves opposite, oblong, sessile or clasping, armed; flowers, numerous,

small, yellow. The latex, while similar to that of *L. Canadensis*, is not as abundant. *L. Scariola* lacks the strong characteristic odor noticed in its relative. Found abundantly throughout Eastern United States flourishing under the most adverse conditions. Although regarded as an unimportant weed by Darlington in his "American Weeds and Useful Plants," published in 1847, it has spread through the greater part of the pluvial portion of the United States, and is now regarded as one of our most troublesome weeds. It thrives upon soils regardless of their lack of plant food or moisture. This plant is often mistaken for "Sow-thistle" (*Sonchus*), commonly known as "Hungarian Lettuce."

The latexes of these plants contain rubber, a waxy acetone soluble body [resin(?)], and a substance of acid nature soluble in weak alkalies, and of intensely bitter taste.

COMPOSITION OF LATUCA LATEXES

	<i>Lactuca canadensis</i> Per cent	<i>Lactuca scariola</i> Per cent
Resin(?).....	11.42	12.85
Rubber.....	2.19	1.58

Rubber.—The quality of the rubber obtained from both these species is exceptionally good, being very firm and strong. There seems to be very little difference in quality between the two products. In quantity the latex of the native species is the richer. In preparing these rubbers, it was necessary, on account of the presence of the acid-like substance, to heat the crude acetone precipitate with boiling alcoholic potash or to precipitate directly the benzole rubber solution with this reagent, and then purify the resin extract.

Resin.—The purified acetone extract is a brittle, light brown substance of waxy feel, and slight bitter taste. Soluble in acetone, alcohol, glacial acetic acid and benzole.

Organic Acid(?)—Insoluble in hot water; insoluble in acetone; soluble in weak alkalies to a fine cherry-red solution. Intensely bitter taste; characteristic plant odor.

Lactuca Canadensis contains, according to Maisch,¹ a bitter principle which has been pronounced equal to *lactucarium* of German origin. *Lactucarium* is a recognized drug of the pharmacopoeia, classified as a *sedative* and *diuretic*, and known as "lettuce opium" on account of its medicinal action which is due to *lactucin* or *lactucic acid*.

Lactucarium is an imported drug originating in Scotland, Rhenish Prussia, and France. In Scotland its production is an industry. The combined production of *lactucarium* and *rubber* may be a possible industry for the North Temperate Zone.

AKRON, OHIO

A COMPARATIVE STUDY OF THE COMPOSITION OF HOPS GROWN IN DIFFERENT PARTS OF THE WORLD²

By H. V. TARTAR AND B. PILKINGTON

In the markets, hops grown in different parts of the world sell for different prices. In this country

¹ A. J. P., 1869, p. 145.

² Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913.

New York hops usually sell at a higher figure than Pacific Coast hops. In the autumn of 1911, while Oregon hops were selling for 40 to 45 cents a pound, New York hops sold for 55 cents a pound and the Saaz hops imported from Europe sold for more than \$1.00 a pound.

Upon observing such a condition as this, one is naturally led to ask: Why all this difference in price? Is the composition of hops from one locality so widely different from those of another locality as to make them have so much greater value for brewing purposes? Does the climatic conditions of different countries so vastly affect the actual value of hops?

The writers tried putting such questions as these to men who had been long engaged in hop growing and buying. In response, various and often very conflicting answers were received. The answers obtained from different brewers were quite as much at variance. In fact, out of all the answers received to our questions, there were not two that exactly agreed. The data obtained would not permit of any definite conclusion, except that people of long experience in the commercial valuation of hops were widely at variance, and no doubt, in many instances, governed by prejudice.

Consequently, in the autumn of 1911, a chemical study of hops from various localities was begun, the object of the study being to ascertain what differences there are in the composition of hops grown in different parts of the world. The samples of Oregon were selected by chemists from this laboratory and were representative. Doctor Alfred C. Chapman, a British chemist who has carried on extensive hop investigations, selected the English samples. We are indebted to Mr. Paul Weidner, Sr., an experienced and reliable hop dealer of Detroit, Michigan, for the samples of Washington (state) hops and also the two samples of Saaz hops. Mr. E. Clemens Horst, who grows hops extensively in the state of California, secured the samples of Californians. At the suggestion of the Director of the New York Agricultural Experiment Station (at Geneva, N. Y.), Mr. E. J. Conger, of Waterville, New York, was employed to select the samples from that state. Doctor A. J. Leheder, of the Pabst Brewing Company, at Milwaukee, selected the samples of Wisconsin. All the samples were as representative as could be secured in this way from the different localities from which they were chosen.

The samples were taken soon after the hop harvest and were analyzed within a few weeks after reaching the laboratory. Meanwhile, they were carefully stored in a cold, dry room to prevent any marked changes in composition from taking place.

Because of the nature of the literature on the chemical composition of the hop, it may be well to state, by way of explanation, that investigators are agreed that the principal constituents of the hop cone are: a volatile oil, a hard resin commonly designated as the "gamma" resin, two soft bitter resins designated as the "alpha" and "beta" resins, a wax, and a tannin. The constituents designated as resins are not true resins,

but owing to the common use of the term in this connection, the authors have continued its use. The recent work of Siller¹ indicates that the gamma resin may be composed of two different substances, but the work is hardly conclusive and we believe needs further study. Recent investigations show that the major part of the actual brewing value of hops lies in the content of soft bitter resins. These substances give to the hop its preservative and flavoring qualities. The volatile oil and tannin may be of minor value in the commercial uses of the hop. It is quite generally conceded by the different authorities on the subject that the hard resin and wax possess no value so far as the brewing industry is concerned.

In the analytical work, the methods which have been worked out in this laboratory² for the determination of the hard, total, and soft (bitter) resins were employed. The separation of the alpha and beta bitter resins was carried out according to the method

It will be noted that there is a somewhat wide variation in the amount of moisture in the samples. This is perhaps due to the fact that some of the samples were stored in a dry storeroom a little longer than others and dried out somewhat. The writers have found that the amount of moisture in hops does not vary widely and is usually between 6 and 10 per cent.

The results show that the genuine Saaz hops have no seeds. The amount of seeds in the New Yorks and Wisconsin samples is not large. In the case of the English samples the range is from 6.15 to 12.50 per cent. The samples of Pacific Coast hops contained from 4.86 to 18.35 per cent. Examinations made in this laboratory of samples of Oregon hops, other than the samples here reported, show a high percentage of seeds.

The amount of extraneous matter found gives an indication of the care taken in picking the hops in different localities. For example, the Saaz samples were free leaves and stems and the English and Wis-

COMPOSITION OF HOPS GROWN IN DIFFERENT PARTS OF THE WORLD. PERCENTAGES

NAME OF LOCALITY	Moisture	Total resin	Total soft bitter resin	Hard gamma resin	Beta resin	Alpha resin	Wax	Tannin	Seeds	Leaves and stems
Washington (state).....	3.90	17.55	15.64	1.91	14.85	0.79	0.37	2.02	4.86	5.0
New York No. 1.....	2.40	14.20	12.81	1.39	8.92	3.89	0.60	1.30	2.50	15.4
New York No. 2.....	3.10	13.89	12.59	1.30	8.91	3.68	0.68	1.95	2.34	15.0
New York No. 3.....	4.10	18.51	16.61	1.90	13.81	2.80	0.71	3.06	0.06	9.0
New York No. 4.....	4.90	16.06	14.20	1.86	11.01	3.19	0.72	2.73	1.84	18.6
California No. 1.....	3.40	17.31	15.08	2.23	11.61	3.92	0.48	2.04	14.75	3.8
California No. 2.....	3.70	17.10	15.72	1.38	11.65	4.07	0.52	2.52	18.35	8.8
California No. 3.....	5.10	12.29	10.79	2.32	4.43	5.54	0.40	1.52	8.38	9.0
California No. 4.....	5.70	15.76	14.10	1.66	9.14	4.96	0.33	1.40	7.55	13.5
Wisconsin.....	4.00	15.82	8.68	7.14	7.93	0.75	not determined	2.40	0.22	1.8
England (Worcester).....	2.50	12.21	9.97	2.24	6.60	3.37	0.50	1.16	9.55	1.2
England (East Kent).....	2.50	11.70	10.51	1.19	7.30	3.21	0.47	1.58	7.90	0.9
England (Sussex).....	4.10	12.70	10.35	2.35	6.05	4.27	0.44	2.22	6.15	0.6
England (Farnham).....	4.80	12.34	11.06	1.28	6.65	4.41	0.39	1.66	12.50	0.0
Oregon No. 1.....	6.30	18.35	16.75	1.60	10.56	6.19	0.33	1.67	11.50	7.6
Oregon No. 2.....	9.20	18.12	16.54	1.58	10.36	6.11	0.37	2.64	11.17	7.2
Oregon No. 3.....	8.87	18.57	16.57	2.00	8.27	8.30	0.37	2.97	13.56	6.2
Oregon No. 4.....	6.80	19.80	17.62	2.18	9.48	8.14	0.41	1.99	1.42	4.0
Saaz No. 1.....	6.50	16.25	14.19	2.06	7.20	6.99	0.54	not determined	none	none
Saaz No. 2.....	8.20	13.75	12.60	1.15	7.62	4.98	0.45	not determined	none	none

outlined by Siller.³ Chapman's⁴ method was used for the determination of tannin. Moisture was estimated by drying *in vacuo* over sulfuric acid at room temperature. The determination of wax was made incident to securing the solutions necessary to the determination of the total resins. The extract obtained by extracting the hops with ether was taken up with alcohol, and the wax, insoluble in this solvent, was collected on a tared filter, washed with alcohol, dried at room temperature and weighed. Owing to the exceedingly small amount of volatile oil present and the consequent difficulty of making a quantitative determination, the estimation of this constituent was omitted. Determinations of the amounts of seeds and extraneous matter (leaves, stems, etc.) were also made.

Other analyses (except in the case of the Wisconsin samples) than those reported in the following table have been made, but the general relationships were about the same as in those here recorded and the analytical data are omitted to economize space.

consin samples contained less than 2 per cent. These results indicate that great care is taken in gathering the hops in these localities. In the New Yorks the percentage of extraneous matter varies from 9 to 18.6 per cent. Evidently these hops had been picked in a very careless manner, since some of them contain more leaves and stems than any other samples the writers have examined. The amount of extraneous matter in the Pacific Coast hops ranges from 3.8 to 13.5 per cent. Other examinations made of our Coast hops show wide differences in the amount of foreign matter in the product put out by different growers. The results show that the percentage of leaves and stems is a matter that should receive much consideration in the correct valuation of hops for commercial use.

The content of soft bitter resins in the different samples is perhaps the most interesting of the results obtained, because of the great importance of these constituents. The Saaz, which demand such high prices in our markets, are somewhat lower in content of soft bitter resins than either the New York or Pacific Coast hops. The English samples are some-

¹ *Zig. Untersuch. Nahrung-Genuss.*, **18**, 241.

² *This Journal*, **4**, 209 (1912).

³ *Loc. cit.*

⁴ *J. Inst. Brew.*, **13**, 646 (1907); **15**, 360 (1909).

what lower in soft resin content than the Saaz samples. The Pacific Coasts, as a rule, have a higher percentage of soft resins than the New Yorks, English or Saaz. These results, with others which have been obtained throughout a series of investigations, lead the writers to believe that the Oregon grown hops have as great, if not greater, average content of soft bitter resins than hops grown in any other part of the world. The sample of Wisconsin contained a high percentage of hard worthless resin. Owing to the fact that only a very small amount of hops is grown in that state, it has not been possible to secure further samples to find out if this is generally true of the hops from that locality.

The variation in the amount of wax is from 0.33 to 0.71 per cent. The content of tannin seems to vary widely, considering the amount present, even in samples from the same locality. These variations in the amounts of tannin and wax, however, are perhaps of little significance, since the wax is of no value and the tannin is perhaps of only minor value.

On the whole, the results indicate that hops which are now holding a superior position in our markets are in reality inferior in composition compared with other hops which are rated lower commercially; this is especially true of hops from certain localities in Europe.

CHEMICAL LABORATORY
AGRICULTURAL EXPERIMENT STATION
CORVALLIS, OREGON

A CRITICAL STUDY OF THE FACTORS CAUSING THE MODIFIED BABCOCK TO RUN LOWER ON ICE CREAM THAN THE ROESE-GOTTLIEB METHOD

By J. O. HALVERSON

Received February 26, 1913

PURPOSE.—The need of a rapid and simple volumetric method for the determination of fat in sweetened dairy products has been shown.¹ This is necessary for a rapid, more accurate fat control test for the ice cream trade, which has now grown to an extensive industry, and is also needed because of the more rigid enforcement of the pure food laws. Such an ice cream test is needed by the food control chemist as well as the manufacturer.

It is the purpose of this investigation to give this proposed test an exhaustive and critical study to determine what fat losses occur and where they occur, thus causing this method to run lower than the Roese-Gottlieb. This would also give more data on the manipulation and factors affecting the accuracy of this test.

It has been shown¹ that the Modified Babcock method averages 0.6 low with the Roese-Gottlieb method. The variation in the fat readings due to temperature and meniscus have been eliminated by using the standard temperature 130° to 140° F. and by the use of glymol.

The low per cent reading of the fat column is chiefly due to the following factors which will be considered.

FACTORS CAUSING LOW FAT READING

1. Residual fat in bulb solution.

¹ THIS JOURNAL, 5, 403.

2. Residual fat in drained-off acid-sugar solution.
3. Per cent of graduation on the test bottles, reads low.
4. Volatile fatty acids lost.
5. Loss of glycerol.

FACTORS CAUSING HIGH FAT READING

1. Impurities in the fat column.
2. Per cent of graduation on the test bottles reads high.

Comparison of the Per cent Fat Found by the Modified Babcock and Roese-Gottlieb Methods on Sample 11/19/12.—Determinations run by the Modified Babcock method on sample No. 11/19/12, with charges taken at different times, were always checked at the same time by the Roese-Gottlieb method. Any variation in withdrawing charges, therefore, from the sample are given in Table I.

TABLE I.—PER CENT FAT FOUND BY THE MODIFIED BABCOCK AND ROESE-GOTTLIEB METHODS. SAMPLE 11/19/12

Detn. No.	Modified Babcock		Roese-Gottlieb method	Calculated reading
	Direct reading	Standard reading		
1.....	16.25	16.15	17.07	17.28
2.....	16.30	16.30	16.91	...
3.....	17.25	17.10
4.....	16.85	16.80
Av.....	16.66	16.59	16.99	...
5.....	16.85	17.00	16.45	...
6.....	16.80	16.60	17.18	...
7.....	16.75	16.50	16.75	...
8.....	16.90	16.75
Av.....	16.83	16.71	16.79	...

Two sets of quadruplicate tests were run under normal conditions (Table I). Determinations 1 to 4 on a preliminary set; determinations 5 to 8 on a second set, of which both direct and standard readings were taken. These determinations in both sets were checked at the same time by the Roese-Gottlieb method to obtain the absolute per cent of fat. Thus the first set of determinations was checked by three Gottlieb tests, one of which was lost. The second set was likewise checked by three tests by the same method. The determinations by the Roese-Gottlieb method vary somewhat, due to the difficulty of obtaining uniform charges on samples which have stood several days. However, the averages of each set of standard readings by the Modified Babcock run low by 0.40 and 0.08 per cent. This tendency on eight determinations averages 0.24 per cent and is only 0.4 as great as found from a larger number of determinations in a previous paper.

LOSSES AND GAINS AFFECTING THE ACCURACY OF THE FAT COLUMN

Residual Fat Lost in Acid-sugar Solution Drawn Off.—This consists of the fat held in the acid-sugar solution which is drained off and lost but not that which adheres to the glass of the bulb. This fat from the acid solution was thrice extracted with anhydrous ethyl ether in a separatory funnel, the ether distilled off and the fat weighed to constant weight, drying in half-hour periods. The fat was then dis-

TABLE II—SHOWING THE PER CENT FAT FOUND AND LOSSES RECOVERED

Detn. No.	Total pure fat			Found in neck			Fat loss in drain and in bulb				Total fat lost in proceedings		Total fat in determination	
	Fat from detn. of impurities	Per cent pure	Per cent impurities	Fat left in neck	Total fat in grams	Fat per cent	In first drain	Per cent	In bulb	Per cent	Fat in grams	Per cent	In grams	Per cent
1.....	1.1995	98.0	2.00	1.6538	2.8533	15.85	0.0552	0.31	0.0731	0.406	0.1283	0.713	2.9816	16.57
2.....	1.3094	98.7	1.30	1.5491	2.8585	15.88	0.0526	0.29	0.1004	0.558	0.1530	0.950	3.0115	16.73
3.....	1.5936	1.3530	2.9466	16.37	0.0264	0.185
4.....	1.7349	98.4	1.60	1.2131	2.9480	16.38	0.1055	0.59	0.0310	0.190	0.1365	0.761	3.0845	17.14
5.....	1.6032	1.3277	2.9309	16.28	0.0323	0.18	0.0446	0.248	0.0769	0.428	3.0078	16.71
6.....	1.4583	1.4347	2.8930	16.07	0.0495	0.275	0.0402	0.223	0.0897	0.498	2.9911	16.62
7.....	1.6207	1.2858	2.9065	16.147	0.0431	0.239	0.0393	0.22	0.0824	0.459	2.9889	16.61
8.....	1.4759	1.4466	2.9225	16.236	0.0412	0.229	0.0504	0.28	0.0916	0.509	3.0141	16.75
Average of detns. 5-8 inclusive							0.0415	0.231	0.0436	0.243	0.0852	0.474

solved out with petroleum ether distilling below 60° C. The residue was dried to constant weight at 70° to 80° C. and the per cent fat calculated. This method was the same as used in a previous paper.¹

In the second set in determinations 5 to 8, of two sets in quadruplicate (Table II), the loss in the first drain in milligrams averages 41.5 and of the first set a maximum of 105.5 or 0.231 and 0.59 per cent, respectively. In determination 4, a slight amount of fat may have been drained off causing this abnormality.

Fat Remaining in the Bulb Solution below the Fat Column.—A slight amount of fat remains in the bulb solution as in the cream tests.²

This solution was drawn off through the glass stopcock after charges of fat from the neck had been taken for determining the per cent of impurities in the fat column. The fat held in solution was then extracted with anhydrous ethyl ether as given above. This recovered fat did not include that adhering to the glass which was estimated with that remaining in the neck.

The following results on the second set, determinations 5 to 8, were obtained (Table II): an average of 43.6 mg. or 0.243 per cent. In the preliminary set, one determination, which is abnormal, gave 100.4 mg. or 0.558 per cent. These results agree closely with the per cent of fat recovered from the acid-sugar solution.

Errors in Calibration Causing the Graduation to Read High or Low.—Another loss (or gain) that occurs is the error in graduation causing high or low readings. The graduation on the four modified test bottles used were standardized by the official method—using the average of three trials.

ERRORS OF CALIBRATION CHECKED BY MERCURY METHOD

Test bottle No. 1, per cent low, average.....	0.305
Test bottle No. 2, per cent high, average.....	0.206
Test bottle No. 3, per cent high, average.....	0.088
Test bottle No. 4, per cent low, average.....	0.235

The error of graduation lies within, except test bottle No. 1, the limits adopted by the Bureau of Standards, viz., the lowest division on the bottle, 0.25 per cent. The error in test bottle No. 1 lies slightly above this limit.

The proportional per cent error for the fat column obtained was then calculated.

This is shown in Table III which is found to be 0.20, 0.161, 0.052, and 0.039 per cent low, respectively, for determinations 1, 4, 5, and 8. Also the per cent reading high are respectively 0.137, 0.062, 0.034, and 0.015 for determinations 2, 3, 6, and 7.

TABLE III—SHOWING EFFECT OF LOSSES AND GAINS ON ACCURACY OF THE TEST

Detn. No.	Fat loss, in first drain	Per cent fat in bulb	Error of graduation per cent low	Total per cent low	Per cent reading high, due to impur.	Error of grad. per cent high	Total per cent reading high	Total per cent low or high
1.....	0.31	0.406	0.200	0.916	0.323	..	0.323	..
2.....	0.29	0.558	..	0.848	0.212	0.137	0.349	..
3.....	..	0.185	0.388	0.062	0.450	..
4.....	0.59	0.190	0.161	0.941	0.269	..	0.269	..
5.....	0.18	0.248	0.052	0.480	0.390	..	0.390	—0.090
6.....	0.275	0.223	..	0.498	0.376	0.034	0.410	—0.088
7.....	0.239	0.22	..	0.459	0.375	0.015	0.390	—0.069
8.....	0.229	0.28	0.039	0.548	0.380	..	0.380	—0.168
5-8 Av..	0.231	0.243	0.046	0.496	0.380	0.025	0.393	—0.104

The average per cent of error in the fat column reading is 0.046 per cent low and 0.025 per cent high on 4 determinations each.

Loss of Volatile Fatty Acids.—Another possible loss is that of volatile fatty acids caused by adding a large excess of acid causing too high a temperature, at which the sulfuric acid may act on the less stable butter fats. While this loss is estimated by the Reichert-Meissl number and the calculations are based on several variable factors, for comparative results these are sufficiently accurate. The molecular weight, 100.7, of the volatile fatty acids, assuming that 87 per cent of the amount present was distilled over in the Reichert-Meissl number, was used throughout. With the exception of the molecular weight, these are the numbers used by Hunziker in his exhaustive investigation on Babcock cream testing.

Sample 12/14/12 was used throughout for this experiment. The loss of volatile fatty acids was estimated by rendering the pure fat in the ice cream and running the Reichert-Meissl number both on the pure fat and that from the neck of the test bottle. The loss of volatile fatty acids would be small. Extra precautions were therefore taken to run the Reichert-Meissl number carefully—being an arbitrary method. The results by this method checked within 0.44 per

¹ THIS JOURNAL, 5, 403.

² Ind. Exp. Sta., Bull. 146, p. 569.

¹ Lewkowitsch, '09 Ed., Vol. I, p. 674.

TABLE IV—SHOWING THE PER CENT OF VOLATILE FATTY ACIDS LOST IN THE MODIFIED BABCOCK TEST IS NEGLIGIBLE

Vol. acids Detn. no.	Fat from neck Detn. no.	Reichert-Meissl No.				Loss of volatile fatty acids		
		Ice cream, per cent fat	In pure fat of ice cream	In fat column of test	Difference	Loss Per cent	Calculation of error due to loss	Per cent error of reading
5.....	(9-14)	16.15	27.55	27.17	0.38	0.014	$16.15 \times 0.0138/100$	0.002
6.....	(9-14)	16.15	27.55	27.17	0.38	0.014	$16.15 \times 0.0138/100$	0.002
7.....	(15, 16, 19)	16.38	27.55	27.39	0.16	0.006	$16.38 \times 0.0058/100$	0.001
8.....	(17, 20)	17.28	27.55	27.14	0.41	0.015	$17.28 \times 0.0149/100$	0.003
17.....	(9-14)	16.15	27.55	26.60	0.95	0.035	$16.15 \times 0.0345/100$	0.006
18.....	(9-14 and 15, 16, 19)	16.24	27.55	26.81	0.74	0.028	$16.24 \times 0.0276/100$	0.005
Average.....						0.019		0.003

cent on 6 determinations of the pure fat. A variation of over 0.5 would give, for the loss in volatile fatty acids, considerable range in results.

The fat in the test bottle from the fat column was given an extreme test by using that obtained from the experiment on the per cent of impurities in the fat column, after having extracted with ethyl ether and dried to constant weight. Odor of volatile fatty acids on drying at 60° to 80° C. is given off, showing there was a slight loss of these acids.

For the determination of Reichert-Meissl number, the fat from two or more of the above determinations was combined. The degree the fats had been acted upon by heat and acid was indicated by the color of the fat itself, by the per cent impurities obtained in the fat column, also by the color of the fat column itself. These observations were used as guides in making up sufficiently large samples for this experiment. Hence fat from determinations 15, 16 and 19 from the experiment for per cent impurities in the fat column (Table V) were combined in one sample, likewise determinations 9 to 14, also 17 and 20.

The average Reichert-Meissl number of 6 determinations on the pure fat is given. The variation on the 6 determinations is 0.44. On the fat from the neck of the test bottle this variation in the Reichert-Meissl number was greater, being 0.79. The per cent loss of volatile fatty acids varied from 0.014 to 0.035 or an average of 0.019 percent. Calculated to per cent error of reading in the fat column, this gives from 0.006 to 0.001 or an average of 0.003 per cent. It was observed that in running the Modified Babcock test, the odor of volatile fatty acids was seldom detected unless the solutions became very hot. These data agree with the observations and shows that the loss of fatty acids is negligible.

The loss of glycerol, according to theory, would therefore be very small in amount and insignificant.

Impurities in the Fat Column.—It has been shown¹ that the fat column does not consist entirely of pure fat; that the impurities consist chiefly of sulfuric acid and water. For cream testing this averaged 1.38 per cent impurities and 98.62 per cent pure fat.¹

On the two sets of quadruplicate tests, all determinations in this experiment but Nos. 1, 2, and 4 were lost. To obtain the standard reading of the fat

column, alcohol was used to eliminate the meniscus and then read at once. On withdrawing charges from the neck with a 5 cc. pipette for the determination of per cent impurities, the alcohol was apt to interfere. It was, therefore, necessary to obtain an average and the variation in the percentage of impurities of a number of determinations, which average for per cent impurities could be used in checking up the gains and losses in this modified test.

Sample 12/14/12 was used and the charges pipetted out from the neck of the test bottle. The charges of 2 to 2.3 grams were weighed into S. & S. thimbles, first placing in 1 to 2 grams of dried precipitated calcium carbonate wrapped in fat-free filter paper. Then small rolls of Adams fat extraction paper, loosely rolled together, were inserted in the thimbles. The fat was weighed by difference onto these rolls. Particular care was taken to leave about 1/2 inch of the fat column in order to guard against the mixture of the liquid below with the fat.

The thimbles were dried 3 hours to constant weight, then extracted from 4 to 6 hours with water-free ethyl ether.

The ether was evaporated off, and the fat dried to constant weight by half-hour periods.

The per cent impurities in the Modified Babcock test ranged from 1.30 to 2.63 per cent. This causes an error in the fat reading varying from 0.21 to 0.43 per cent high. Determinations 17 and 20 ran high, 3.97 and 3.24 per cent, respectively. On 14 determinations an average of 97.73 per cent pure fat and 2.27 per cent impurities causing 0.387 per cent error in the fat reading was found.

Some data were obtained on the approximate amount of sulfuric acid and water present (Table V). The loss of water on drying gives the data necessary for calculating the per cent of acid and water. The amounts present appeared to bear no relation to each other.

The per cent impurities in the fat column is somewhat higher than found in cream testing by Hunziker. This appears reasonable as the color of the fat column is a light walnut-yellow, not the usual golden yellow. If a large excess of acid is used, the impurities in the fat column increase as in determinations 17 and 20 above. Therefore, the directions for adding acid should be closely adhered to.

¹ Hunziker, Ind. Exp. Sta., Bull. 145, p. 565.

TABLE V—SHOWING IMPURITIES CONTAINED IN FAT COLUMN OF THE MODIFIED BABCOCK AND RESULTING ERROR IN READING THE TEST

Detn. No	Modified Babcock Per cent	Analysis of fat column					Calculations of error of reading due to impurities	Error of reading	
		Per cent fat	Per cent im- purities	Impurities in fat					
				Mg. H ₂ SO ₄	Mg. H ₂ O				
1.....	16.15	98.0	2.00	Total imp.	24.6	16.15	$\times 2.0$ 100	0.32	
2.....	16.30	98.7	1.30	Total imp.	16.4	16.30	$\times 1.30$ 100	0.21	
4.....	16.80	98.4	1.60	Total imp.	29.1	16.80	$\times 1.60$ 100	0.27	
9.....	16.15	98.1	1.90	28.0	10.7	16.15	$\times 1.90$ 100	0.31	
10.....	16.02	98.45	1.55	7.5	27.0	16.02	$\times 1.55$ 100	0.25	
11.....	15.90	97.99	2.01	17.3	18.5	15.90	$\times 2.01$ 100	0.32	
12.....	16.10	98.11	1.89	35.6	2.3	16.10	$\times 1.89$ 100	0.32	
13.....	16.25	97.97	2.03	18.2	21.1	6.25	$\times 2.03$ 100	0.33	
14.....	16.50	97.51	2.49	27.5	26.3	16.50	$\times 2.49$ 100	0.41	
15.....	16.50	97.44	2.56	Total imp.	68.1	16.50	$\times 2.56$ 100	0.42	
16.....	16.25	97.44	2.56	Total imp.	66.4	16.25	$\times 2.56$ 100	0.42	
17.....	18.20	96.03	3.97	Total imp.	94.5	18.20	$\times 3.97$ 100	0.72	
19.....	16.25	97.37	2.63	19.4	41.1	16.25	$\times 2.63$ 100	0.43	
20.....	16.35	96.76	3.24	17.4	63.1	16.35	$\times 3.24$ 100	0.53	
14 detns., averaging	97.73	2.27							0.387

EFFECT OF LOSSES AND GAINS ON THE ACCURACY OF THE TEST

The summary of all the preceding data is given in Table III. In determinations 1 to 4 in the preliminary set, some of the data were inaccurate. Only the data of value are given.

In the second set, determinations 5 to 8, the total losses of fat range from 0.459 to 0.548 per cent. The total gains of fat range from 0.380 to 0.410 per cent. In balancing the average loss, which includes the various factors influencing the accuracy of the fat column, against the average gain due to other factors, a balance of 0.104 per cent low is obtained.

This furnishes additional weight to strengthen the opinion that the chief factors influencing the accuracy of the fat column have been considered.

Per Cent Fat, the Fat Column Should Read.—From the data given in Table III, the per cent of fat, the

TABLE VI—PER CENT FAT COLUMN READS WITH ALL LOSSES AND GAINS ACCOUNTED FOR

Detn. No.	Per cent total fat recovered	Error in gradu-ated neck	Per cent read- ing high due to im-purities	Cor-rected fat column test then reads	Per cent fat, Roes-ottlieb method
1.....	16.57	+0.20	+0.323	17.095	17.07
2.....	16.73	—0.137	+0.212	16.942	16.91
3.....	17.31	—0.062
4.....	17.14	+0.161
5.....	16.71	+0.052	+0.390	17.152	16.45
6.....	16.62	—0.034	+0.376	16.962	17.18
7.....	16.61	—0.015	+0.375	16.970	16.75
8.....	16.75	+0.039	+0.380	17.169

columns in determinations 5 to 8 should read with all losses and gains accounted for, can be calculated. The results are given above in Table VI.

The corrected fat columns of the Modified Babcock compared with the per cent of fat found by the Roes-ottlieb method check closely. In the first set, these results varied from 17.07 to 16.91 per cent while the Gottlieb method on the same sample in the first set gave 17.09 to 16.94 per cent. The corrected results then fall well within the per cent obtained by the R. Gottlieb method.

In the second set, determinations 5 to 8, the corrected fat columns then read 17.169 on determination 8, down to 16.962 per cent on determination 6, while the corresponding per cent on the check samples varied between 17.18 and 16.45 per cent. Thus all the corrected fat columns lie between the per cents found by the Roes-ottlieb method. This also substantiates the above results.

UNCOMPENSATED FAT LOSSES WHICH CAUSE THE MODIFIED BABCOCK METHOD TO RUN 0.6 PER CENT LOWER THAN THE ROESE-GOTTLIEB METHOD

TABLE VII—SHOWS THE UNCOMPENSATED LOSSES WHICH CAUSE THE MODIFIED BABCOCK TO RUN LOWER THAN THE ROESE-GOTTLIEB METHOD

Detn. No.	Fat lost in first drain Per cent	Fat in bulb Per cent	Total fat lost Per cent
1.....	0.31	0.406	0.716
2.....	0.29	0.558	0.848
3.....	0.185
4.....	0.59	0.190	0.780
5.....	0.18	0.248	0.428
6.....	0.275	0.223	0.498
7.....	0.239	0.22	0.459
8.....	0.229	0.28	0.509
Average of detns.....	0.302	0.288	0.605

In Table VII are shown losses of fat which occur over and above the per cent fat indicated by the reading of the fat column. The fat column itself, however, reads high on account of the impurities it contains. The reading, though in the neck of the test bottle, of the per cent fat in the ice cream sample is low by the amount of that which is lost in the drawn-off acid-sugar solution and by the per cent held in the bulb solution below the fat column.

In seven determinations, 1 to 8, the average per cent lost in the first drain is 0.302. The fat contained in the liquid in the bulb below the fat column averages 0.288 per cent. The total per cent uncompensated fat lost is an average of 0.605. This result agrees with the per cent the Modified Babcock reads low on 44 determinations run on 3 samples of ice cream which were compared with the Roes-ottlieb method.

CONCLUSION

Below are briefly summarized three sets of proof which tend to show that the work is accurate and rationally accounts for the low fat readings by this proposed test.

I. A summary of the factors causing small losses and gains of fat affecting the accuracy of the fat column in the second set of determinations 5 to 8 were given in Table V. The total losses and gains due to these various influences check each other closely (—0.104 per cent).

¹ A previous paper, "The Modified Babcock for Fat in Sweetened Dairy Products—Ice Cream."

II. In Table VII are shown what the fat columns, when corrected for these losses and gains of fat, should read. These results were then compared with those for per cent fat obtained by the Roesse-Gottlieb method. Barring some variation due to the non-uniformity of the charges themselves, the reading of the fat column, according to calculations, agrees very closely with the results found by the Roesse-Gottlieb method.

III. Further, Table VIII gives a summary of the losses of fat in the acid-sugar solution and in the bulb solution which losses are the cause for the low per cent of reading of the fat column. The average per cent fat loss is 0.605. On the second set, determinations 5 to 8, the average is 0.474 per cent. It is obvious that these losses of fat in the Modified Babcock are almost twice as great as in cream testing. Thus multiplying the average fat loss 0.28 per cent, in cream, as found by Hunziker, by 2 and comparing this with twice the amount of fat drained off, 0.256 per cent, gives approximately the same fat loss as found in the Proposed Modified Babcock test.

SUMMARY

The above facts warrant the following conclusions:

1. That the same factors obtain as in cream testing with one exception, that of draining off the acid-sugar solution involving a fat loss of 0.258 per cent.¹

2. The loss of volatile fatty acids is insignificant, having no effect on the accuracy of the fat reading. The same is true of glycerol.

3. The per cent impurities in the fat column in this proposed test is higher than in cream testing because the conditions under which the end point is worked out are somewhat different. The darker color of the fat column itself also substantiates this.

4. Uncompensated losses of fat are caused by the fat lost in the first drain, the acid-sugar solution, and in the bulb solution. This loss is approximately twice as great as in cream testing.

MISSOURI DEPARTMENT OF FOOD AND DRUG INSPECTION
COLUMBIA

TINCTURE OF IODINE²

By L. F. KEBLER

This commodity has probably been examined more frequently than any other simple drug offered for sale by the retail trade, and I know of no medicinal agent which has more frequently been found wanting. Observations and investigations have frequently shown that when iodine was dissolved in simple ethyl alcohol there was a great tendency for the iodine to be changed into hydriodic acid and other compounds thus actually lowering the free iodine content and the diminution increased with the age of the preparation. Experiments conducted to obviate this difficulty indicated that the presence of potassium iodide tended to inhibit the usual combination of the iodine and thus increase the stability of the tincture. The method outlined for the manufacture of this commodity by the last (8th) revision of the U. S. Pharmacopoeia pre-

scribes the use of a certain amount of potassium iodide. The shortcomings of the tinctures available on the market have, however, not been materially reduced. Almost every state board which has taken up this question has found that a large number of the samples are deficient in iodine content. This shortcoming cannot now be so fully ascribed to deterioration, neither can it be ascribed to difficulties in manufacture because the process of manufacture is extremely simple.

During the past few years a considerable number of samples of tinctures of iodine have been examined in the Bureau of Chemistry. The samples shipped into interstate commerce were found to comply closely with the pharmacopoeial requirements. All of them contain the requisite amount of potassium iodide. A goodly number of samples were collected in the District of Columbia and analyzed with the following results:

ANALYSIS OF TINCTURE OF IODINE

IODINE		POTASSIUM IODIDE		ALCOHOL	
Grams per 100 cc.	Per cent variation(a)	Grams per 100 cc.	Per cent variation(a)	Per cent volume	DECLARATION
1.97	71.5	1.3	74	86	Correct.
3.42	50	None	100	93.5	Not declared.
4.40	36	5.38	7.5	85	" "
5.04	27	None	100	94.4	" "
5.08	26	3.03	40	95	Small type.
5.09	26	Trace	100	91	Correct.
5.36	22	2.1	58	95	" "
5.52	19.5	5.30	6	95	Not declared.
5.57	19.5	5.84	17	93.5	" "
5.81	15	5.03	None	93.5	Correct.
5.88	14.5	None	100	95	Not declared.
5.89	14.5	None	100	92.8	" "
6.06	12.5	6.82	36	94.5	Correct.
6.09	11	1.02	80	93.5	Not declared.
6.11	10	4.93	1	95	Correct.
6.18	10	5.37	7	91	" "
6.18	10	4.45	11	93	" "
6.24	9	4.32	13.5	88	" "
6.29	8	2.79	46	91	Not declared.
6.29	8	4.61	8	91	Small type.
6.32	8	2.58	48.5	91	Not declared.
6.34	7.5	None	100	93.6	Small type.
6.36	7.5	3.84	23	93.5	Not declared.
6.48	5.5	4.92	2	95	Correct.
6.48	5.5	3.81	24	88.5	" "
6.49	5.5	5.34	7	95	Small type.
6.73	0.5	6.52	30	95	Correct.
6.75	0.5	2.42	51.5	96	" "
6.76	0.5	3.82	24	85.5	Small type.
6.78	...	2.46	51	90.5	Correct.
6.80	...	3.95	21	91	Not declared.
6.80	...	3.49	30	86.5	" "
6.84	...	5.56	11	93	Incorrect.
6.85	...	5.1	2	92.72	Correct.
6.90	...	0.97	80.5	95	Small type.
6.97	0.5	None	100	91.5	" "
7.00	2.0	5.79	16	91	Not declared.
7.03	2.5	5.52	10	91	Small type.
7.04	2.5	5.00	None	93.5	Correct.
7.18	4.5	4.58	8.5	89.5	" "
7.21	4.5	5.17	3	90.5	" "
7.21	4.5	5.67	13.5	88.50	Not declared.
7.24	5.5	5.14	3	90	" "
7.58	10.5	5.12	2	94.5	Correct.
7.95	15.6	4.50	10	86	Not declared.
8.07	17.5	4.38	12.5	90	Small type.
8.11	18	3.86	23	91.50	Not declared.
8.11	18	6.00	20	95	Correct.
8.37	21.9	5.45	9	89	Not declared.
9.26	35	5.23	4.5	89.5	" "

(a) N. B.—The per cent variation in the above analyses is calculated to the nearest half per cent.

¹ THIS JOURNAL, 5, 403.

² Read before the City of Washington Branch American Pharmaceutical Association, February 12, 1913.

The pharmacopoeial tincture contains about 6.86 grams of free iodine and 5 grams of potassium iodide in 100 cc. The range of variation (1.97 to 9.26 grams per 100 cc.) is certainly remarkable. What real valid excuse can be offered for either of the above extremes? Furthermore, is there any substantial reason for some of the other variations? The permissible variation from the standard must be met sooner or later. Shall it be stringent or reasonable? If reasonable, shall the variation be 5 per cent or 10 per cent or 20 per cent? Considering that the adjective "about" qualifies the amount of free iodine that should be present in the tincture, about 60 per cent exceed a 5 per cent variation, 40 per cent a 10 per cent variation and 18 per cent a 20 per cent variation. I do not believe many manufacturers will contend for or advise a 20 per cent variation in that it would not only savor of carelessness but actually encourage it. Is then a 10 per cent variation either way from the standard, reasonable, fair and just to the manufacturer, the consumer, the physician, etc., or is it desirable to be more stringent?

Suggestions are invited either in the columns of THIS JOURNAL or otherwise. The free iodine is the essential factor of this tincture but the potassium iodide and percentage of alcohol must also be considered. The conditions noted above relative to the variability of the free iodine also hold for potassium iodide. The variation ranges from no potassium iodide to 6.82 grams per 100 cc. Discussion in this connection is also invited.

DRUG DIVISION
BUREAU OF CHEMISTRY
U. S. DEPARTMENT AGRICULTURE

THE APPLICATION OF FOLIN'S METHOD FOR THE DETERMINATION OF AMMONIA TO FERTILIZERS

By OTTO FOLIN AND A. W. BOSWORTH

Received March 3, 1913

The determination of ammonia in commercial fertilizers is usually made by distilling with magnesium oxide.¹ In Folin's method for the determination of ammonia in urine² the ammonia is removed by a strong air current at room temperature. This method is generally applicable to all kinds of materials and has the advantage of being both rapid and reliable. It has been used for the determination of ammonia in meat³ and in cheese.⁴ The speediness of the determination has been greatly increased by the micro-chemical modification recently published by Folin and Macallum.⁵ By this new method an ammonia determination can be made in less than half an hour. This method is applicable to the determination of ammonia in fertilizers. Applied to such products the method is as follows:

Two grams of fertilizer are placed in a 100 cc. graduated flask, about 50 cc. of water added, and then 25 cc. of approximately normal hydrochloric

acid. The volume is now made up to 100 cc. with water, the contents of the flask are shaken, and after standing a few minutes are shaken, a second time. The flask is now allowed to stand until the heaviest of the undissolved particles have settled. Five cc. of the supernatant liquid are withdrawn by means of a pipette (filtering is not necessary) and transferred to the tube of the Folin apparatus. Two cc. of a saturated solution of potassium oxalate, a few drops of kerosene and finally 2 cc. of a saturated solution of potassium carbonate are added. The apparatus is immediately closed and air passed through for 10 to 20 minutes. The ammonia is collected in a flask or test tube which contains 20 cc. of seventieth normal hydrochloric acid. If the air current is produced by a blast the ammonia is collected in a flask and 25 cc. of water are added to the 20 cc. of acid in order to increase the volume and thus prevent the loss of ammonia. After the distillation, the contents of the flask, or test tube, are titrated back with seventieth normal sodium hydroxide, using alizarin red as indicator. The percentage of nitrogen as ammonia is found by subtracting the number of cubic centimeters of alkali used from the number of cubic centimeters of standard acid used, and dividing the difference by five.

Diagrams of the apparatus with descriptions have been given by Folin and Farmer.¹

The method as given has been tried on several samples of fertilizers and the results obtained, together with those obtained by the magnesium oxide method, are given in the table below. The two sets of results were obtained by different persons, working in different laboratories and the results by the Folin method were obtained several months after those by the magnesium oxide method.

The samples are representative of what may be found on the market.

Sample number	NH ₃ by the Folin method	NH ₃ by distilling with MgO	Total nitrogen	Chief source of nitrogen
1	0.00	0.00	2.10	nitrate, organic
2	0.08	0.05	3.20	" "
3	0.11	0.06	8.24	" "
4	0.03	0.08	5.11	" "
5	0.03	0.13	1.51	organic
6	0.08	0.13	5.25	nitrate, organic
7	0.20	0.17	2.07	" "
8	0.06	0.17	1.13	organic
9	0.22	0.20	3.43	nitrate, organic
10	0.15	0.20	3.09	" "
11	0.29	0.38	3.13	" "
12	0.31	0.39	2.46	" "
13	0.43	0.42	1.09	organic, ammonia
14	0.70	0.65	4.71	nitrate, organic, ammonia
15	0.69	0.77	2.83	" ammonia
16	0.90	0.89	2.29	organic
17	1.04	1.07	2.16	nitrate, organic, ammonia
18	1.37	1.38	2.58	organic, ammonia
19	1.47	1.44	3.99	nitrate
20	1.48	1.59	4.02	" organic, ammonia
21	2.31	2.33	4.07	organic, ammonia
22	2.72	2.58	3.08	" "

¹ Bureau of Chemistry, U. S. Department of Agriculture, *Bull.* **107** (revised).

² Folin, *Z. physiol. Chem.*, **37**, 161.

³ Pennington and Greenberg, *J. Am. Chem. Soc.*, **32**, 561.

⁴ Bosworth and Winter, Bureau of Chemistry, U. S. Department of Agriculture, *Bull.* **152**.

⁵ Folin and Macallum, *J. Biol. Chem.*, **11**, 523.

BIOCHEMICAL LABORATORY
HARVARD MEDICAL SCHOOL
BOSTON

¹ Folin and Farmer, *J. Biol. Chem.*, **11**, 493.

LABORATORY AND PLANT

THE USE OF NATURAL GAS IN STEAM BOILERS¹

By GEORGE W. BARNES

This use of natural gas is possibly the earliest in the history of this most valuable, yet until recently least valued, fuel provided by nature. In many localities the supply was seemingly inexhaustible with the natural result that only cost of installation was considered and efficiency was never determined if even thought of.

The introduction of this fuel into the commercial field did not, for years, suggest a reasonable valuation; millions of cubic feet were furnished daily to Pittsburgh and other localities, and sold to industrial plants for steam boiler use at a flat rate per H. P. rating, no attention being given to the installation or the quantity used, this being left entirely to the consumer; in many localities, notably through the mid-continent field, this practice prevails to-day. As a result, types of burners and methods of installing were almost as numerous as the installations. Each engineer had his own opinion, seldom, if ever, based on either experience or knowledge of the use of gas or its application. A few of the novelties would not be credited to-day; for instance:

1. Rows of Bunsen burners under the shell (Return Tubular Boiler) starting at the front of fire box and spaced eighteen inches apart extending the full length of the boiler.

2. An open pipe flame in the fire box and a similar flame introduced at the back and driven into the tubes, the result being a red-hot stack at times of heavy load.

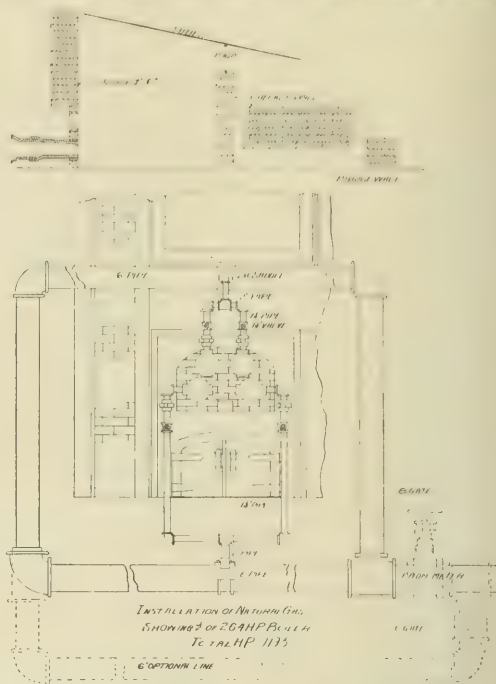
The usual method of early installations was the perforated pipe burner introduced in various forms; this gave good results as a steam generator, but was extremely wasteful, some later tests showing an efficiency as low as twenty to twenty-five per cent and few if any reaching fifty per cent.

The first burner observed by the writer to be designed for this work by a well defined knowledge of the requirements was the "Whysall;" this consisted of a series of well designed Bunsen tubes, built into the side walls of the fire box, the flames striking across the fire box, meeting at the center where they were broken up; any unconsumed carbon escaping the primary combustion was supplied with air admitted through the fire doors, making a practically perfect combustion of the gases before reaching the bridge wall. This type in various forms was used for several years and good results were obtained.

The type in use for the past ten or twelve years and one that has best met the requirement of the many varied conditions is the tubular burner. This is made in several forms differing only in minor details, and in fact has become the standard for water tube and return tubular boilers. These burners are carefully designed and when properly installed give perfect results. In installing, care should be given to pipe and fittings, and ample capacity should be provided.

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

This should be sufficient to supply the gas to the burner at a pressure of from three to five ounces, allowing



for an overload of from fifty to sixty per cent of boiler rating. The accompanying sketch shows a good general plan of installation.

SUMMARY OF SIX TESTS MADE IN WATER TUBE BOILERS (a)

Kind of flame.....	White	Blue
Number of 250 H. P. boilers used.....	6	6
Average gas pressure at burners, ounces.....	6	6
Cu. ft. of gas used when reduced to 4-ounce pressure and 60° F.....	626815	561638
Equivalent water evaporated at and from 212° F.....	496163	441963
Average boiler H. P. made.....	1597.7	1423.2
H. P. made per 250 H. P. boiler.....	266.3	237.2
Cu. ft. of gas reduced to 4-ounce pressure and 60° F. used per boiler H. P. per hour.....	43.6	43.8

(a) Extract from paper prepared for the American Society of Mechanical Engineers, by Jay M. Whitham.

In operating it has been found that the best results have been obtained where the long straw white flame is used (note test made by Mr. Whitham, for example): in addition, the checker wall or a modification of same has been found absolutely necessary as the flame must come in immediate contact with an incandescent surface to insure a perfect combustion within the zone of usefulness. This system has been used almost exclusively for years.

While the use of natural gas for steam boiler work has not reached anything like the efficiency that has been obtained from its use in other industrial work or in domestic appliances, it by no means follows that it could not be greatly improved; in other industrial

RESULTS OF GAS BURNER TESTS AT WEST VIRGINIA UNIVERSITY ENGINEERING LABORATORY

Number of test.....	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Date, 1906.....	1/27	2/10	2/13	2/16	2/17	2/22	2/23	2/24	3/3	3/10	3/16	3/17	3/21	3/24	3/27	3/30	3/31	4/3	4/6
Duration in hours.....	5	5	3	5	5	5	5	4	5	5	4	5	5	4	5	5	5	5	5
Color of flame.....	Color-less	Color-less		Colorless, with blue streaks	White with blue streaks	White, with blue streaks	Colorless	White	White	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Steam pressure in boiler by gauge.....	120	120	121.5	121	122	123	122.5	121.5	120.5	121.5	121.5	120.5	121.0	120.5	121.0	120.5	121.0	120.0	119.5
Gas pressure outlets, above atmosphere.....	7	5	8	5	8	3	5	5	8	5	6	5	5	5	5	5	5	5	5
Gas pressure, in. mercury.....	0.9	0.64	1.0	0.64	1.0	0.4	1.0	0.4	1.0	0.4	0.76	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Draft, in. water.....	0.15	0.15	0.45	0.45	0.45	0.44	0.48	0.50	0.40	0.45	0.40	0.45	0.47	0.40	0.40	0.40	0.40	0.40	0.40
Barometric pressure, in. mercury.....	29.10	29.51	29.15	29.54	29.35	29.26	29.16	29.15	28.66	29.00	29.04	29.52	29.63	29.28	29.38	29.06	29.06	29.06	29.06
Temperatures, degrees F:																			
Feed water.....	45.5	39.0	40.0	38.4	38.0	37.9	38.0	38.3	41.2	41.5	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Gas at meter.....	53.8	48.0	49.0	47.4	48.3	48.7	50.4	48.9	51.5	50.5	46.5	48.5	48.6	62.0	65.5	73.2	76.3	76.3	76.3
Pile.....	239	229	261	250	269	273	273	279	265	262	262	267	267	245	280	207	213	207	207
Boiler room.....	64.4	53.0	66.5	59.8	69.0	68.0	75.5	74.5	75.8	69.5	65.0	70.0	70.0	84.0	89.4	93.0	93.0	93.0	93.0
Pounds of water evaporated per hour from and at 212° F.	4151	2861	5711	4734	6248	6003	6390	6600	6010	6075	6686	6599	6327	3778	2344	3007	4086	4086	4086
Quality of steam in per cent.....	85.0	80.0	89.0	86.7	93.0	96.0	97.0	96.5	96.3	95.6	95.8	96.1	94.7	82.0	95.5	81.4	80.2	80.2	80.2
Boiler Horse Power.....	126.0	89.0	172.6	142.7	184.7	175.9	186.5	193.2	176.0	178.9	196.0	187.5	186.2	116.1	145.0	120.5	126.2	126.2	126.2
Cubic feet of standard (32° F. -29.95) gas per hour.....	5632	4204	7247	6126	8044	7185	8109	8593	7999	7672	8689	7209	7116	5121	7212	5585	5778	5778	5778
Cubic feet of standard gas per pound of water evaporated from and at 212° F.....	1.35	1.47	1.27	1.29	1.28	1.19	1.26	1.30	1.31	1.27	1.30	1.12	1.12	1.36	1.37	1.43	1.42	1.42	1.42
Cubic feet of standard gas per Boiler Horse Power.....	44.4	41.1	42.1	42.8	43.5	40.8	43.4	44.4	45.4	42.8	44.5	38.4	38.2	44.1	40.5	46.3	45.8	45.8	45.8
Total B. T. U.'s per cubic ft. standard gas.....	1110	1143	1144	1098	1156	1143	1116	1029	1124	1108	1071	1134	1136	1100	1100	1057	1088	1088	1088
Available B. T. U.'s per cu. ft. standard gas.....	1040	1060	1056	1015	1056	1064	1039	992	1046	1018	983	1052	1050	1051	1051	918	935	935	935
Efficiency of boiler in per cent.....	67.1	61.9	69.2	71.0	66.0	71.2	68.8	70.7	65.3	70.2	70.2	76.7	76.8	68.6	65.8	69.4	66.9	66.9	66.9
With steam jet in burners.....	Yes	Yes	No	No	No	No	Yes	Yes	No	No	Yes	Yes	Yes	No	No	No	No	No	No
Flue gas analysis, per cent by volume:																			
Carbon dioxide—CO ₂	8.90	6.80	8.20	7.70	8.50	5.20	8.96	8.07	8.00	8.26	9.26	8.00	8.53	6.52	8.00	8.40	8.80	8.80	8.80
Oxygen—O.....	4.30	7.10	4.50	6.80	3.70	4.70	3.60	3.60	2.70	4.06	4.26	6.00	5.15	8.90	3.00	4.60	4.40	4.40	4.40
Carbon monoxide—CO.....	0.00	0.40	0.10	0.00	0.30	0.23	0.08	0.83	1.70	1.00	0.56	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00
Nitrogen—N.....	86.80	86.70	87.20	85.50	87.00	86.87	87.36	87.50	87.60	86.68	85.92	86.00	86.54	84.88	88.00	87.00	86.80	86.80	86.80
Excess air.....	22.5	45.3	24.1	42.7	18.9	25.4	18.3	18.2	13.0	21.3	23.0	35.4	28.7	65.5	14.6	24.7	23.4	23.4	23.4

and domestic uses, furnaces and appliances have been designed and constructed best adapted to the use of gas, many having a sustained efficiency of eighty-five to ninety per cent, while all steam boilers are constructed with a view to the use of coal as fuel.

In the use of gas, from seventy to seventy-five per cent efficiency is about the maximum sustained.

In the tests made at the West Virginia University under the direction of Prof. C. R. Jones, very practical results were obtained, showing what can be done in continuous work. By making allowance for difference in heat value of gas to be used, the cost of steam can readily be obtained.

To compare with coal costs, allowance should be made for the following items, in addition to coal on track: cost of handling to grate bar, ash removal, repairs, grate bars, linings, tube cleaning (return tubular), and additional oil, boiler repair, overamount when gas fired, cleaning machinery (resulting from coal and ash dust), value of overload (short or long) possible with gas, value of automatic regulation and constantly uniform steam pressure under all loads; all this must be determined and added to cost of coal or deducted from cost of gas before one can fairly and accurately compare relative costs.

A detailed consideration of this subject would require the description of as many various applications as there are plants, as no two can be installed the same in all details, location of plant with reference to physical surroundings, conditions of fire room, stack draft, nature and type of boilers, setting, constant or variable load, the type of man who superintends the steam plant—all must be considered in making a success of the use of gas.

PITTSBURG, PA.

A VITRIFIED CLAY COMBUSTION TUBE WITH TAPERED OUTLET FOR THE DETERMINATION OF CARBON IN STEELS, FERRO ALLOYS AND GRAPHITE

By CHARLES MORRIS JOHNSON
Received May 15, 1913

The wide-spread use of the vitrified clay combustion boat introduced by the writer in 1909 ("Analysis of

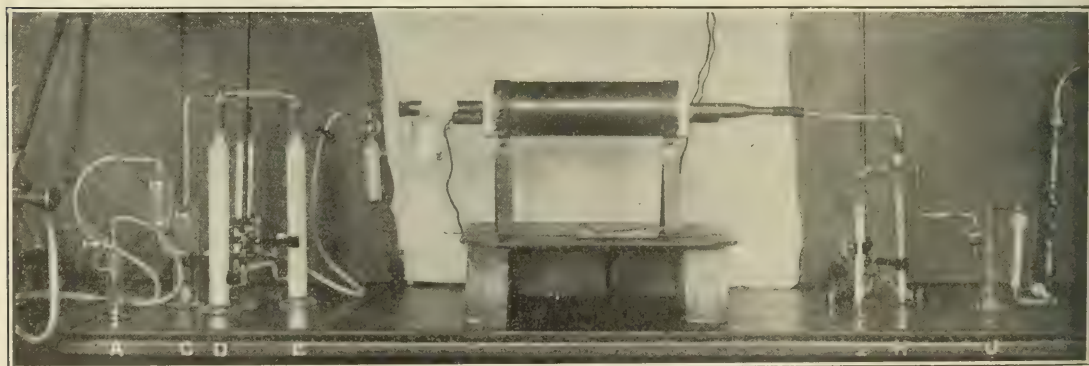
After considerable experimenting a tube has been produced which has been in service night and day for several weeks and at this writing is still running, giving perfect results.

It has been the object of the author to produce a tube that will not be so readily slagged with basic material which is the extremely weak feature of the now almost universally used silica tube. The latter is of course entirely acid in its nature. The amount of experimenting that can be done along this line will be very considerable and much time must necessarily elapse before the most perfect composition can be reached, hence the writer wishes to establish priority at this stage of the work. The good service already obtained by the author with the tapered clay tube (shown in the illustration), which is of simple and most inexpensive composition, inspires confidence that the days of the costly combustion tube for iron and steel works carbon determinations are numbered.

The taper design for clay ware combustion tubes is original with the author and it has the advantage of reducing the rubber stopper nuisance fifty per cent. The combustion train is also shown as it is now connected, and filled. J is the weighing apparatus. The oxygen enters the safety jar C containing liquid KOH, then passes through the soda lime in E, next it travels up through D which contains anhydrous calcium chloride; it then crosses over and down through stick KOH contained in the jar in the rear and from thence into the little valve tube attached to the rubber stopper. This mercury valve serves a double purpose of absorbing sulfur coming from the rubber tubing and prevents any possibility of CO₂ being forced in the wrong direction.

The entire train and furnace with the exception of the tapered clay tube, is essentially the same as when first published in May, 1908 (*J. Am. Chem. Soc.*, **30**, 773).

The writer desires to acknowledge the assistance of Mr. Bayard Guthrie, of Park Works, Crucible



Special Steels, Steel-making Alloys and Graphite," Jno. Wiley & Sons, 1909) suggested to the writer the possibility of making an inexpensive combustion tube of similar material.

Factory, in preparing the apparatus necessary to work the clay into shape.

THE LABORATORY OF THE PARK WORKS
CRUCIBLE STEEL CO. OF AMERICA
PITTSBURG, PA.

AN ELECTRIC DESICCATOR FOR THE ANALYSIS OF INDIA RUBBER AND OTHER ORGANIC COMPOUNDS

By L. J. D. HEALY

Received April 1, 1913

The desiccator herein described was primarily designed by the writer for use in rubber analysis but it might advantageously be used for other lines of organic work. It is simple in construction and inexpensive.

As is well known, the amount of moisture in the various rubbers is an important factor in the manufacture of rubber goods as its presence is apt to cause trouble. In the determination of moisture in rubber, the removal of the last traces of moisture is very difficult on account of its being adsorbed by the rubber colloid and very tenaciously held. For quick moisture

to the nature of the rubber and amount of moisture it contains. It was for the purpose of more rapidly making this determination of moisture and for drying the rubber at various stages of its analysis that this desiccator was designed.

The following sketch illustrates its construction: Fig. 1 shows the details of the apparatus. It consists of an ordinary vacuum desiccator, *A*, containing an electric heating coil, *C*. The coil *C* is made from an ordinary $\frac{1}{2}$ -inch porcelain insulator tube six inches long and fitted with a square piece of fiber at each end as shown. The tube is wound with twelve feet of No. 34 nichrome wire, the latter being secured to two terminals at either end of the coil. Two insulated wires, connected to the terminals of the coil, pass out

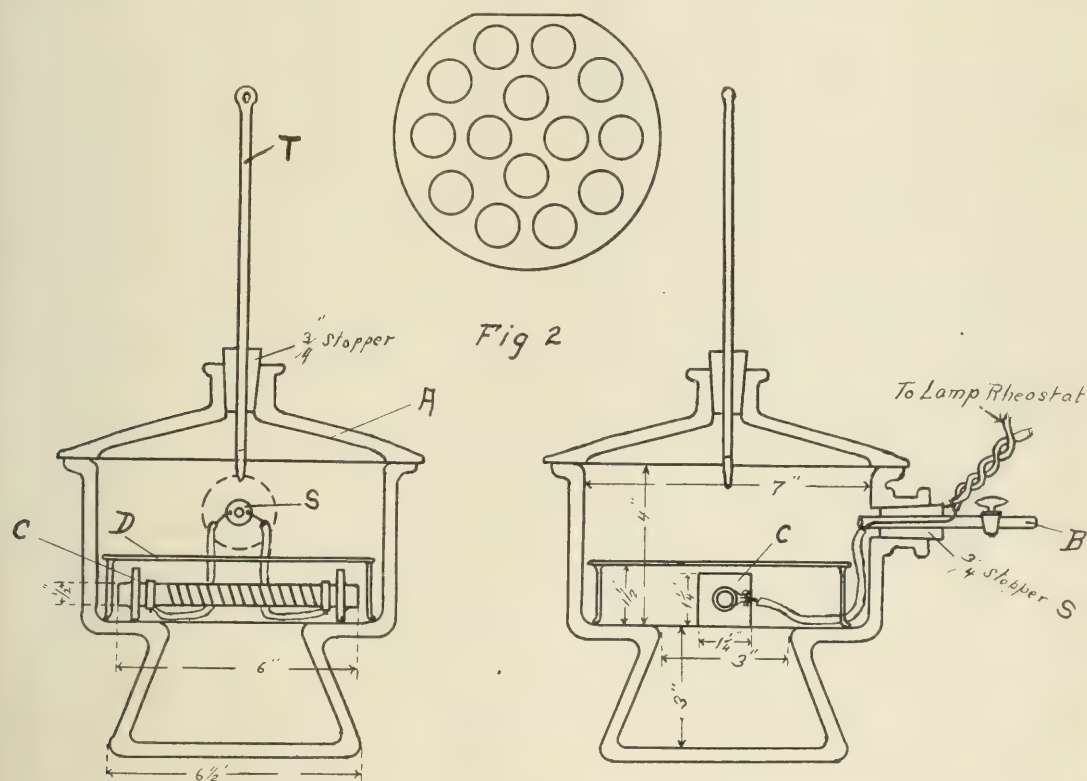


Fig 1

tests which need be only approximate, such as for factory control, the rubber can be dried in air at 100°C . to approximately constant weight, but this method invariably leads to oxidation of the rubber by the atmospheric oxygen. This latter can be avoided by drying the rubber in a stream of illuminating gas at 100°C . but again a serious error results, due to the absorption by the rubber of certain constituents of the gas. The usual method is to place the finely divided rubber on a watch glass in a desiccator and dry over sulfuric acid or calcium chloride *in vacuo*. This method, however, while giving good results, requires from twenty-four hours to a week, according

of the desiccator through the rubber stopper at *S* and are connected by flexible lamp cord to a lamp rheostat consisting of four 16 c. p. incandescent lamps connected in series parallel. The tube *B*, communicating with the interior of the desiccator, is connected by rubber tubing to a manometer and vacuum pump. The tray *D*, for supporting watch glasses, etc., is made of sheet metal to aid in radiation of heat and is shown in detail in Fig. 2. The temperature of the desiccator is controlled by the lamp rheostat. By turning on one or more lamps either in series or parallel, a range of temperature, varying from 45°C . to 175°C . can be obtained. A thermometer, *T*, indicates the tempera-

ture within the desiccator. The lower part of the desiccator is partly filled with anhydrous calcium chloride.

The procedure is as follows: The finely divided rubber is weighed on a watch glass and placed in the desiccator. The air is exhausted and the electric current turned on. Usually one lamp is sufficient and will maintain a uniform temperature of about 60° C. If necessary the temperature may be further reduced by placing two lamps in series. The electric current is left on for one hour and, if during that time the vapor pressure within the desiccator becomes greater than 75 mm., the stopcock at *S* is opened and the vapor exhausted. At the end of one hour the electric current is turned off and the desiccator allowed to cool. Air is then slowly admitted and the desiccator is again allowed to stand for some time until the last traces of moisture have been absorbed by the chloride. The rubber is then weighed and the procedure repeated until the weight of the rubber is constant. For control purposes, one heating is usually sufficient.

Very satisfactory results have been obtained with this type of desiccator in the analysis of rubber and compounding ingredients used in the manufacture of rubber goods. The removal of the air prevents oxidation and the heat produced by the coil, while not enough to injure the rubber, is sufficient to rapidly vaporize the water at the prevailing pressure within the desiccator. For soft rubbers a thin sheet of dried asbestos may be placed on the tray *D*, to reduce the radiation of the heat from the coil. The following tables offer a fair comparison between the ordinary type of vacuum desiccator and the electrically heated desiccator and give some idea of the time saved.

TABLE I—MOISTURE DETERMINATION ON GUAYULE

Ordinary vacuum desiccator		Electric vacuum desiccator	
No. hours	Per cent moisture	No. hours	Per cent moisture
40.....	23.6	1.....	20.2
64.....	28.5	2½.....	31.3
88.....	30.1	3½.....	33.0
136.....	32.2	4½.....	33.5
160.....	32.8		
184.....	33.1		
208.....	33.3		

TABLE II—CONGO RUBBER

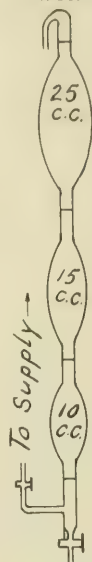
Ordinary vacuum desiccator		Electric desiccator	
No. hours	Per cent moisture	No. hours	Per cent moisture
24.....	0.84	2.....	0.98
48.....	1.02	3.....	0.98
72.....	1.02		

As shown in Table I, one portion of a sample of crude guayule approached constant weight after 208 hours when dried in an ordinary desiccator, against 4½ hours for a portion of the same sample dried in the electric desiccator. Again, Table II shows that a sample of Congo required 72 hours for check weight against 3 hours when dried in the electric desiccator.

A COMPACT, ACCURATE BURETTE FOR USE IN NITROGEN WORK OR WHENEVER MANY MEASUREMENTS OF STANDARD ARE NECESSARY

By FRANK C. GEDBACH

Received April 8, 1913

RUSSELL SAGE INSTITUTE OF PATHOLOGY
NEW YORK

The accompanying drawing illustrates a burette devised for use, primarily, in Kjeldahl work but applicable in all lines of work where it is necessary to make repeated measurements of standard solutions. The burette consists of three bulbs, blown without shoulders and delivering 25, 15, and 10 cc., respectively. Two portions of 25 cc. each may be drawn without refilling, or likewise 10, 15, 40 or 50 cc. From the top meniscus mark to the lower measures 6½ inches, thereby placing each meniscus in easy reading distance without rising to adjust the zero. The stopcocks are provided with borings at the end through which is driven a small piece of wood in front of which has been placed a small rubber washer, thereby rendering "lifting" impossible. This burette may be secured from Eimer & Amend, New York City.

A COMBINATION APPARATUS STAND

By E. R. SQUIBB & SONS

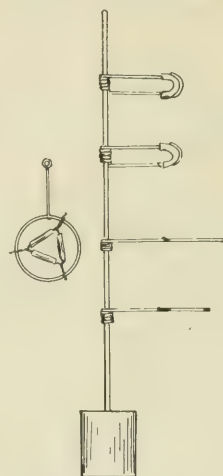
Received April 15, 1913

This device has been in use in the research laboratory of E. R. Squibb & Sons for some time and has

proven very satisfactory in practice.

The apparatus consists of a nickel-plated, upright rod, about 22 inches in height and ¼ inch in diameter, secured in an iron cylinder base weighted with lead. Several attachments, adapted for various chemical manipulations, can be fitted to the rod.

These proposed attachments consist of (see drawing) spring clamps which slide closely over the rod and lock automatically by binding on the same. A clamp is easily shifted up or down or swung sideways by a slight pressure.



The advantage over other such stands is its stability, neat appearance and compactness. The stand is simple, portable and can be used for many simultaneous operations. Its uses are:

1. For filtering (can hold four or more funnels).
2. For holding burettes absolutely rigid, and perpendicular, permitting them to be easily moved up or down. Each stand may hold 2 or more burettes

which are movable around the axis of the rod.

3. For supporting light condensers.
4. For holding separatory funnels.
5. For supporting crucibles and small beakers.

After using, the apparatus can be set aside and occupies no more space than an ordinary reagent bottle. This is of importance where space is a factor.

BROOKLYN, N. Y.

ADDRESSES

PRODUCTION AND INDUSTRIAL APPLICATION OF BY-PRODUCT COKE OVEN GASES¹

By J. BECKER AND L. B. ROBERTSON

In a paper covering the production and industrial applications of coal gases you will all appreciate that this subject can be treated only in a general way, without taking up more than the allowed time. We shall therefore attempt to briefly outline the process of distillation of coal and the treatment and application of the resulting gases.

The first distillations of coal were performed in bee-hive ovens for the purpose of making coke. No gas is recovered from this coke-making process, and the only application of the gas produced is its combustion in the bee-hive oven over the coal in order to supply the heat and maintain the temperature necessary for the coking process. Then coal was distilled in retort ovens, for the recovery of illuminating gas. Coal is charged into these retorts and the liberated gas collected in a so-called hydraulic main. The gas next passes through a washing and purifying system and is collected in gas holders from which it is distributed to consumers, either for illuminating or household purposes. These retorts vary in size as well as in their position in the retort benches: horizontal, vertical and inclined retorts are in present use; the coal coked in these retorts must be of a very high grade, in order to produce the best gas. Usually the desired candle power of the gas governs the quality of the coal to be used. The fuel necessary to perform the distillation of coal consists of a part of the coke produced by this gas-making process.

The first chamber ovens were waste heat ovens, and, like bee-hive ovens, were built for the sole purpose of producing coke from coal. We call them chamber ovens to distinguish between this type and other types of ovens and retorts. The chamber oven is built in the form of a long, narrow chamber varying in size from 4 to 15 tons capacity. The division walls between these chambers contain flues in which the gas produced from the distillation of the coal is burned so as to maintain the temperature necessary for the coking process. The gas received from waste heat ovens passes through openings in the top of the oven chamber and from there burns downward through the flues. Air necessary for the combustion of this gas is admitted from the outside. The waste gases from these ovens have a high temperature and are often utilized under waste heat boilers for generating steam.

There are also built, especially in England, the Mond Gas producers. Low-grade coal is charged into these producers and the gas received is used for heating purposes after recovering the ammonia and tar. A large amount of steam is introduced in order to keep the gasifying zone at a low temperature to prevent decomposition of the ammonia formed. The amount of ammonia recovered from this process amounts to about 20 to 80 pounds in form of ammonium sulfate. The recovery of the by-products makes this process a very economical one.

Competition, and the desire to produce gas and coke most economically, brought an oven on the market, which, we are sorry to say, is not by any means used enough in this country

at the present time for making gas and coke. This is the By-Product Coke Oven. Long ago the wasteful bee-hive ovens disappeared from the plants of the coke and gas manufacturers in Germany. The by-product coke or gas oven is a chamber oven with a capacity of about 5 to 15 tons of coal per oven chamber. These ovens are built in batteries varying from 25 to 70 ovens per battery. The division walls between the ovens serve as heating walls and contain either vertical or horizontal flues in which the combustion of the gas takes place. In the improved by-product coke and gas ovens, the air used for the combustion of the fuel gases is preheated in recuperators or regenerators placed under the oven chambers. The products of combustion of the fuel gases first pass through the recuperators or regenerators in order to heat them and are then collected in a larger flue and discharged through a chimney.

In explaining the process of coal distillation we shall confine ourselves to the chamber oven. The kind of coal to be used depends entirely upon the purpose for which the coal is being coked, whether for the production of gas only, coke only, or both coke and gas. At coke plants, the coke is considered the main product. At gas plants, gas is the main product, and the coke is considered as a by-product. The ideal way would certainly be, to consider both coke and gas as main products, which means making good gas and good coke from a given coal. All this may be done in a chamber oven only, by coking certain coals or mixtures of certain coals. The chamber oven can produce a good illuminating gas as well as a valuable furnace coke, while retorts can produce a good gas but an inferior coke which cannot be used for blast-furnace purposes. The gas manufacturers must use a coal which gives a gas with a certain candle power. It is an undeserved handicap to the gas manufacturer to make gas on a candle power basis, since most of the gas is burned in mantles where the candle power of the gas means little or nothing. For this reason the quality of the gas should be judged on a B.t.u. basis. The Germans have long ago abolished the system of selling gas with a given candle-power. The requirements are certain heat units per cubic meter. Americans, considered as the most progressive people on earth, will undoubtedly do away with this antique law of judging qualities of gas by candle power. If this requirement is done away with, gas, with a good heating value, could be made with an inferior and cheaper kind of coal, which means that gas could be sold cheaper for public service. In order to bring this about, Americans should continue their progress by adopting the mantle universally, which will allow a lower candle power gas to be used.

In the process of distillation, coal is charged into the chambers and the heat for coking this coal is transmitted from the heating flues to the coal charge. The gas evolved from the coal is conducted by means of ascension pipes to the collecting main and from there to the cooling, washing and purifying apparatus by means of an exhauster which forces the gas through the pipes and apparatus into the holder. Immediately after the coal is charged into the oven, coking begins, forming a solid and thick mass on the surface of the coal. This mass on the outside of the charge consists of partly decomposed coal which is heated by radiation from the heating wall. The reversed side of this mass, that is, the side towards the center of the coal charge, is cooled by the coal which lays just behind it. The

¹ Paper presented before the Chicago Section of the American Chemical Society, Hotel Sherman, February 14, 1913.

tar formed from this mass condenses, on account of the cooling effect of the cooler coal behind it, and is redistilled again as the heat travels towards the center of the charge. The coal in the center of the oven stays unchanged until the tar mass has traveled toward the center and in turn is decomposed after it has reached the necessary temperature. In other words, the tar travels in or condenses toward the center of the coal charge, and the gas passes out toward the oven walls and from there along the walls to the ascension pipes. This means that the temperature of the coal in the center of the charge may be very low for many hours, and that this temperature will not raise appreciably until the heat introduced through the oven walls has reached the center. The fact that the tar condenses toward the center of the charge, forming there a tight and solid mixture of coal and tar, proves that the gas must travel from the coal charge through the coke formed, to the walls, and that the gas does not pass through the coal mass; in other words, the gas

tar somewhat, but, due to the redistillation of the tar leaving its carbon, an increased coke yield will be obtained. The amount of gas as well as the amount of coke produced by this process is greater than in retorts.

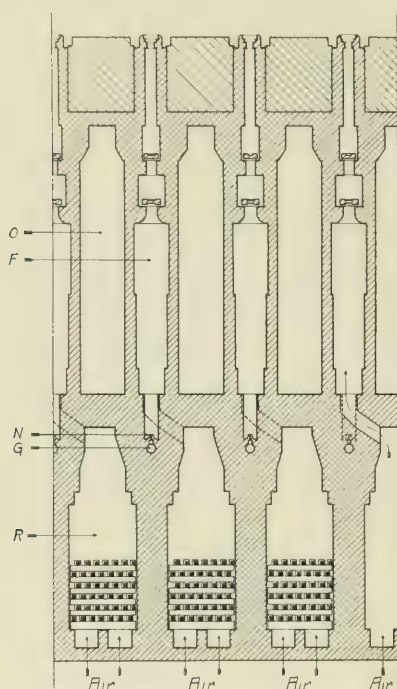
If a given coal is coked in a retort and in a chamber oven, the results will be that from the retorts will be obtained a larger amount of thick, inferior tar containing a high percentage of free carbon and a smaller amount of coke, on account of the carbon which forms on the roof of the retorts, whereas in the chamber oven a larger amount of coke and a smaller amount of light and fluid tar, containing a small percentage of free carbon, will be produced. The gas received from both is in quality practically the same, but the quantity is larger in a chamber oven. The amount of gas produced in the chamber oven is the maximum which can be obtained.

The greatest difference in the principles of the distillation in chamber ovens and in retorts is, that by coking small amounts of coal as is done in retorts, the condensing and redistilling of the tar which takes place in the coking process of chambers does not occur in the retorts. The first formed tar gases cannot condense, but pass along the roof of the retort where they are decomposed, leaving a large amount of carbon as residue. Part of the carbon formed by the decomposition of these tar fumes is carried with the gas into the hydraulic main, where it settles out and becomes mixed with the tar, thus increasing its per cent. of free carbon. In a retort, it is quite necessary to have considerable overhead heated surface, which is the roof of the retort, in order to produce a good gas yield. If this decomposition of the tar gases did not take place, the yield of the gas in the retort would be very low. The residue from this decomposition, the carbon found on the roof of the retort, is recovered in a chamber oven in form of coke, which has some value.

The manner in which the heat is transmitted to the coal charge, as well as the temperature in the heating flues, has a great effect on the quality and quantity of the coke. Coal coked at high temperature usually gives a higher coke and gas yield but a lower by-product yield. The gas received from coal coked at a high temperature, which means in a short coking time, usually gives a gas with a lower candle power, but there is not much change in the heating value per cubic foot. The heating value of total gas produced per pound of coal distilled is higher when coking the coal at high temperatures. The coke received from coking the coal at high temperatures is usually smaller in size than that received by coking at low temperatures.

In order to produce the most uniform coke and gas at any temperature of the heating flues, it is very important to have the heat in the heating walls distributed very uniformly. Thus, the rate of heat transmission to the coal charge is uniform and an even coking of the charge will take place. Overheated or underheated spaces in the heating wall will show up in the quality of the coke. The coke nearer the overheated area will be of smaller size while the coke produced from the underheated area will be undercoked, which means that it still contains uncoked coal particles and consequently too much volatile matter. Overheated areas in the oven walls affect the gas passing over these areas by decomposing the heavy hydrocarbons in the gas thus decreasing the candle power. From the above it is easily seen that for coking coal, only that oven should be used in which the combustion of fuel gases and consequently the transmission of the heat to the coal charge can be controlled in every heating flue. An oven which has many of these flues per heating wall and one in which every flue can be controlled and regulated individually would be the ideal oven to make the most uniform coke and the best gas.

There is one great advantage of the coke oven over the retort. In a coke oven, illuminating gas can be made from a lower grade of coal than in retorts. Or, a high-grade gas coal, giving a poor quality of coke, can be mixed with a low volatile



"A" Koppers Cross Regenerative
Coke Oven.

travels in the opposite direction to the flow of heat. Tests were made on coke ovens in Germany, where coal was coked at a coking time of 30 hours. The coal was charged wet. The temperature of the center of the coal mass did not exceed 100° C. after 15 hours coking. This proves that the action of the heat is not to evaporate the moisture in the entire coal charge first, but is simply to evaporate the moisture of the coal nearer the walls, which moisture condenses toward the center of the mass and gradually evaporates as the heat travels to the center of the coal charge. The moisture remains in the coal during the first period and assists in the gradual condensation of the tar first formed. This is one reason why some coal when charged wet will give a better coke than when charged dry, for the moisture condenses the more heavy tar in the mass, which, after being redistilled, gives the coal the desired bonding substance to form good coke. This may possibly reduce the amount of

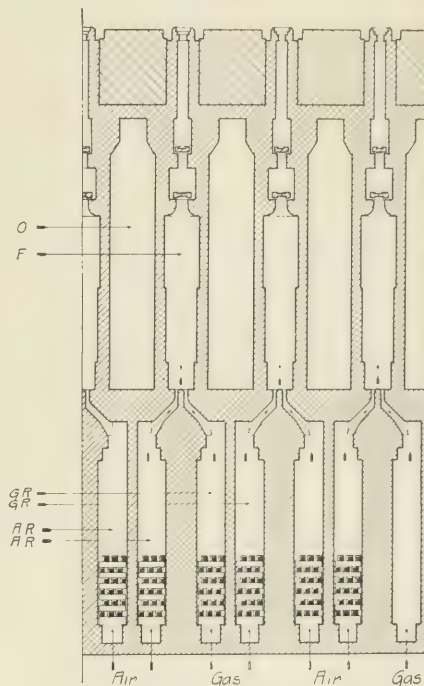
coal giving a high grade of coke. Such a mixture will produce a good coke, suitable for blast furnaces and foundries, and a good quality of illuminating gas. This is done by means of separating the gas received from the coking process. The gas given off from coal during the first 10 hours of the distillation has a higher heating value and a higher candle power than the gas produced towards the end of the process. The first gas may have 16 to 18 candle power and 650 to 700 B.t.u., while the gas received from the second part of the distillation may have 12 to 14 candle power and 560 to 600 B.t.u. These two gases are collected separately by means of two collecting mains, or by one collecting main divided by a longitudinal partition. Each gas passes through a separate washing and purifying apparatus. The gas received from the first part of the distillation, the so-called "rich gas," is sent to the rich gas holder, and that received from the second part of the distillation is burned under the ovens. The amount of each gas depends largely on the quality of the coal charged into the ovens. Also let us say here that ultimate and proximate analysis of a coal does not tell by any means what products would be obtained from the distillation. For determining the coking value of a coal as well as the quality and amount of distillation products, the coal must first go through a distilling process, either in a laboratory or by coking the coal in an oven chamber.

The first process installed for treating the gases was by cooling, washing and purifying. The gas, after leaving the collecting main, passes through a cooler, where it is cooled to about 80° F. The water produced from the coal both from the condensation of the moisture and the water formed from the hydrogen and oxygen of the coal, and the tar is condensed in these coolers. They are usually tubular, the water passing through the tubes and the gas around them. After leaving the coolers, the gas passes through a number of washers, where it is brought in direct contact with water, which absorbs the ammonia in the gas. The gas then passes through boxes containing iron oxide for the removal of hydrogen sulfide and cyanogen and then is led to the gas holder. During the last few years the methods for treating the gases have been very much simplified. It is easily understood that to wash out the ammonia requires an enormous quantity of water, especially in larger plants. Also the floor space taken up by the ammonia washers is enormous. The percentage of the ammonia recovered in these washers depends to some extent on the temperature of the water used. In summer time and especially in places where the temperature of the water supply is high, the washing of the gas is not perfect—losses of 10 per cent. of the total ammonia produced are not unusual.

Being Koppers men, we wish to explain the direct process for treating gases. This process was introduced by the H. Koppers Co., in practically all parts of the world in gas and coke oven plants. After the gas leaves the collecting main it is drawn through tubular condensers, where it is cooled down to the desired temperature. The exhauster then forces the gas through a tar extractor where the last traces of the tar are removed. The gas leaving the tar extractor is naturally saturated with water vapor. After leaving the tar extractor, it passes through a reheater where the temperature of the gas is raised about 15° C. and is no longer saturated for that temperature. It next passes through saturators, containing a saturated solution of ammonium sulfate and about 5 per cent. of sulfuric acid. All the ammonia in the gas is combined with the sulfuric acid in the saturators forming ammonium sulfate, which precipitates out instantly. The salt crystals are removed from the saturator by means of an ejector which discharges into a draining table, and pass from there to centrifugal driers, then to the storage pile. This process works continuously and all the ammonia in the gas is recovered. After the gas leaves the saturators it may be used for any purpose. If used as illuminating

gas it must pass through the purifier and from there to the gas holder from which it is distributed to consumers for household and heating purposes. The sulfate received from this process is perfectly white and contains at least 25 per cent. of ammonia and only 0.1 to 0.2 per cent. of free sulfuric acid. The condensates received from the coolers are collected and the small amount of ammonia water distilled in a still passing the ammonia vapors back into the gas again so that they finally reach the saturators. This direct process is already installed in a great many plants and works with great success. The advantages over the wash processes are:

1. Smaller amount of labor required.
2. Less floor space.
3. No water for washing is necessary.
4. No pumps for wash water.
5. Less steam consumption by the stills.
6. More complete recovery of ammonia.
7. Can be installed in any climate because it is independent of the temperature of water supply.



"B" Koppers Cross Regenerative Gas Oven

The application of coal gases, with which we are all more or less familiar, is in cooking and lighting. We have already explained that with the proper coal, and with the distillation taking place under the proper conditions, the requirements regarding candle power can be easily met. This statement is borne out by the fact that millions of feet of gas for household uses are now produced from chamber ovens and delivered to the consumers in the same condition as it leaves the purifiers.

Among the industrial applications of by-product coke oven gases, we wish to take up its use as fuel for boilers, gas engines, open hearth furnaces, heating furnaces, its various uses in foundries, etc.

By-product coke oven gas has an average heating value of 450 to 550 B.t.u. per cu. ft. Its comparison with other fuels

will be based on a heating value of 500 B.t.u. We shall also assume a coal of 12,000 B.t.u. and fuel oil of 18,000 B.t.u. per pound as a basis of comparison.

By product coke oven gas has proved its value as fuel for open hearth furnaces only in the last five or six years. It is now considered as one of the best fuels for this purpose on account of the higher temperature obtainable, a better economy both in the use of heat and in the construction of the furnace, an increased tonnage and lower operating costs as compared with producer gas.

The gas was first used in the same manner as producer gas, being passed through regenerators before meeting with the preheated air in the combustion chamber. This was found unnecessary, as its high heating value enabled sufficiently high temperatures to be maintained without preheating; besides, the gas actually loses approximately 9 per cent of its heating value by

the checkers was greatly increased. This is due more perhaps to the more skilful handling of the furnace as the workmen become better acquainted with the peculiarities of the gas.

Blast furnace gas is too low in heating value for use as an open hearth fuel, but when mixed with coke oven gas in the ratio of 3 or 4 to 1 volume of coke oven gas, sufficiently high temperatures have been maintained.

The gas required per ton of open hearth product will vary with the size of the furnace and the nature of the charge. For a liberal estimate let us take the results reported from a 4-ton open hearth furnace design for producer gas but now using coke oven gas. In this furnace 880 pounds of coal per ton of product were replaced by 15,400 cu. ft. of coke oven gas per ton, making the gas equivalent of a net ton of coal as open hearth fuel, 35,000 cu. ft.

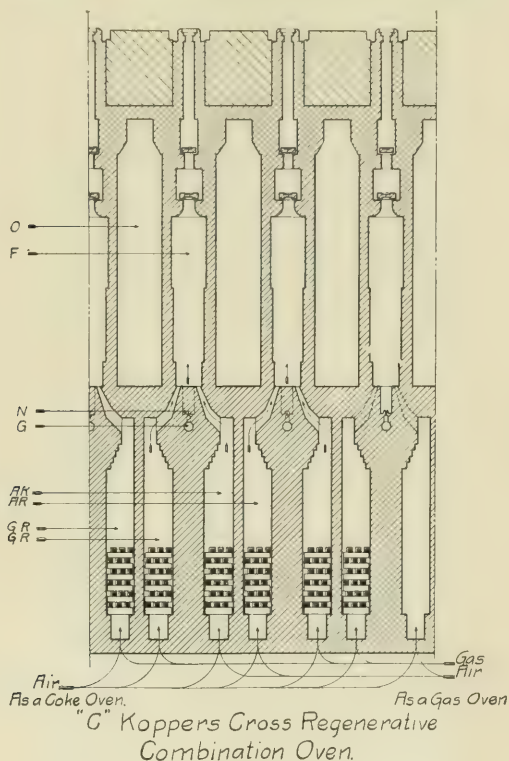
Next to its use as open hearth fuel, coke oven gas is probably best adapted to heating furnaces. Here again the operating cost is reduced and the tonnage of the furnaces greatly increased. The gas required per ton of product varies greatly according to the size of the material to be heated, ranging from 1,500 cu. ft. per ton in large ingot heating furnaces to 33,000 cu. ft. per ton of smaller material, such as bolt and nut rods. Part of this great difference is due also to the ingots being charged directly from the stripper while the small rods are charged cold. In this capacity the gas equivalent of a net ton of coal will average approximately 29,000 cu. ft.

As a boiler fuel, coke oven gas has proved economical for replacing coal. The lower repair and labor costs for gas-fired boilers are just as great a saving as where producers are replaced by coke oven gas. The efficiency of the boiler is also increased approximately 10 per cent. Under a boiler approximately 100 cu. ft. of gas are required per boiler horse power, or the gas equivalent of one net ton of coal as boiler fuel is 35,400 cu. ft.

Since we have no reliable information at present for a comparison of coke oven gas with fuel oil, if we assume that the two fuels are used with the same efficiency, we find the gas equivalent of 1 gallon of oil to be 264 cu. ft.

In the foundry, the coke oven gas adapts itself to various uses, all of which tend to make the work of the foundry lighter and more pleasant and to decrease the cost of the products. In many foundries, where it is available, it has replaced coal and coke as fuel in every use except the cupolas and even there it is often used for kindling. It lends itself very readily to drying molds and ladles, and to firing coke ovens. To these foundry applications already mentioned, must be added the furnaces for melting brass and other alloys as well as pits for crucible heating.

Last, but not least, of the industrial applications of coke oven gas is in the gas engine. It has not as yet come into general use in gas engines, owing principally to the effect of the sulfur and cyanogen compounds upon the piston, the interior of the cylinder, and the valves. These difficulties are overcome by purifying the gas and with rapid improvement in design; there is no doubt but coke oven gas engines will come into common use. Much of the progress in the development of these engines has been made in Germany, where there are many power plants now using by-product coke oven gas in gas engines. One of the most interesting ones of these is described by C. A. Tupper, in *Mining and Engineering World* for Dec. 23, 1911. This plant was located in Rhenish, Prussia, and consisted of two electrical generator stations operated in parallel, one equipped with steam turbines and the other with gas engines operated on by-product coke oven gas. Power was developed by the gas engine with 30 cu. ft. of 500 B.t.u. gas per kw. hr., by the steam turbine with 13.6 pounds of steam per kw. hour. This amount of steam would require in the neighborhood of 40 cu. ft. of gas to develop



preheating. Therefore, the gas is now introduced cold and only the air passed through the regenerators, which allows of smaller regenerators and thus cheaper furnace construction.

On account of the high heating value of this gas a temperature may be maintained considerably higher than with producer gas, allowing a greater tonnage for the furnace. The output in some cases has been known to increase 15 to 20 per cent. Also by using the fuel which is already a gas, operating costs will be reduced by the amount of the operating costs of the producers. It has been claimed by some that the life of the furnace was shortened by the higher temperatures obtained with this gas, also, that the light gas had a tendency to rise and burn along the top of the furnace instead of just over the bath. These difficulties are being rapidly overcome and cases have been cited where the roof has actually stood more heats than with producer gas before repairing was necessary, while the life of

it in steam boilers, to say nothing of losses in steam lines and condenser auxiliaries.

Let us see what we may do with a ton of coal. First we may coke it in a bee-hive oven and get in return 65 per cent or 1300 lbs. of coke with which we may produce something less than 1200 pounds of pig iron.

Again, let us put it in a by-product coke oven. We get in return 1500 lb. of coke which will produce over 1350 lbs. of pig iron, about 17 c. worth of tar, 60 c. (net) worth of ammonium sulfate and still have sufficient surplus gas to replace 286 pounds of coal in the open hearth furnace or under boilers, or produce 224 electrical horse power. In other words, our saving by the by-product ovens over the bee-hive is 200 lbs. of coke, 77 c. worth of tar and ammonia and 224 electrical horse power.

As mentioned before, it is very important to have the best possible heat distribution on the oven in order to get the most by-products in the gas as well as the best coke, and we wish to explain to you a coke oven which has all the features required to obtain this even distribution of the heat. This is the Koppers Regenerative Coke and Gas Oven.

A battery of Koppers regenerative coke ovens (Fig. "A") consists of a series of oven chambers placed side by side. The wall between two ovens serves as a heating wall. This heating wall consists of about 28 to 30 vertical flues in which the combustion takes place. Underneath these vertical flues is a gas distributing flue. Every vertical flue is connected to this gas flue by a gas nozzle through which the gas is introduced into the vertical flues for combustion. These nozzles are interchangeable, so that a nozzle with any desired size of opening can be used. Directly underneath each oven chamber is a regenerator where the air used for combustion in the vertical flues is preheated. It enters the regenerators at the bottom and passes up through the hot checker work and then to each individual flue, where the combustion of the gas takes place. The amount of air admitted to the regenerator can be regulated by means of individual dampers for each oven. During one period the gas burns in one-half of the vertical flues of the oven walls and the products of combustion pass into a horizontal flue which is placed just above the vertical flues and from there to the other half of the vertical flues of the oven walls, then down to the regenerator on the other side, where it gives off its heat to the checker brick and passes into a common flue leading to the chimney. The draft in each regenerator can be regulated by means of a damper at the entrance to the regenerators and in each vertical flue by sliding bricks which are placed at the outlet of each vertical flue just where they connect to the horizontal flue. With these sliding bricks, the combustion in each vertical flue as well as the length of the flame and the draft in each individual flue can be regulated. The setting of these sliding bricks can be regulated through openings from the top of the battery which means that each individual flue can be easily inspected. After the gas is burned on one side for a period of one-half an hour, this process is reversed and the gas is burned in the vertical flues through which the waste gases passed before reversing.

Reversing of gas and air is done automatically by means of cables which are connected to the covers of the individual flue boxes on each regenerator as well as to the gas cocks in the connections leading to the gas distributing flue underneath the vertical flues.

It is easily seen that with this design of oven absolutely uniform heats can be maintained over the entire oven wall, for the operator is able to inspect every part of the oven wall and regulate the combustion accordingly. The amount of gas used to coke a coal in these ovens amounts to but 45 or 50 per cent of the gas produced, a figure which is not reached by any other coke oven construction. The remaining 50 to 55 per cent of the gas produced

from these ovens is received in form of gas and not in form of waste heat, as is the case in some other oven designs where the waste heat is used for raising steam in boilers. By using waste heat for raising steam, the utilization of the B.t.u. is not as economical as when surplus gas is burned under a boiler. By using surplus gas in a boiler, one is able to regulate the amount of gas and air so as to obtain the most efficient and economic operation of the boilers. The temperature of the waste gases after they leave the regenerators on the Koppers ovens is so low that they can be discharged directly through the chimney. The advantage of the regenerators over the recuperators is well known.

In gas plants, where the main product is illuminating gas, and where there is no market for coke, the H. Koppers Co. has constructed a gas oven (Fig. "B") which is similar to the coke oven. Instead of using half of the gas as fuel, all the gas made can be used as illuminating gas, the oven being heated with producer gas. Coke breeze and small coke from the ovens can be utilized as fuel for the producers. The regenerators on the gas ovens are divided into two parts by means of a vertical wall which extends the entire length of the oven chamber and no gas distributing flue connected to the vertical flues is used. The producer gas as well as the air necessary for combustion is preheated in these regenerators and meets in the vertical flues where combustion takes place. The amount of underfiring, that is, the amount of fuel used in the producers in order to gasify the coal in the oven chambers, is much less than that used for gasifying coal in retorts. The amount of underfiring in retorts is 16 to 20 per cent, whereas in Koppers gas ovens it amounts to 10 to 12 per cent. The underfiring, of course, depends to some extent on the kind and efficiencies of the producers installed.

The Koppers Co. has also constructed a combination oven (Fig. "C") which can be used either as a coke oven heated with gas produced in the ovens, or as a gas oven heated with gas generated in gas producers. This oven is similar to the gas oven just described with the addition of the gas distributing flue underneath the vertical flues as on coke ovens. When operating on producer gas, the gas is sent through half the regenerators before entering the vertical flues, which allows the use of all the gas produced in the ovens for illuminating gas. If only half the amount of illuminating gas is desired, this oven can be heated with a separated fuel gas, passing this fuel gas to the gas distributing flue, the air being preheated in all the regenerators. This oven is one of the most flexible ovens ever constructed. A plant having these combination ovens can be first operated as a coke plant by separating half of the gas and using the other half as fuel gas. The plant can be built large enough to operate on a long coking time and with the increase of illuminating gas consumption; the coking time can be lowered gradually so as to produce more gas corresponding to the amount of illuminating gas desired. After the limit of the coking time is reached, then gas producers can be installed and the oven heated with producer gas made from coke breeze. This allows all the gas made in the oven to be used as illuminating gas, and the coking time can be increased again. With the increasing demand for illuminating gas the coking time can be then decreased until the limit of coking time is again reached. A further increase on the demand of illuminating gas naturally would mean building additional ovens.

1307 MALLERS BLDG.
CHICAGO, ILL.

SYNTHESIS OF PRECIOUS STONES¹

By I. H. LEVIN

Our present success in reproducing the precious stones makes

¹ Presented at the meeting of the New York Section of the American Chemical Society, May 24, 1912.

us reflect upon the unsuccessful attempts of the alchemists to produce the precious metals. How much our modern ways differ from theirs! The so-called magic and mysticism of the alchemists have given way to science. Selfish competition and lack of cooperation have given way to accumulation of knowledge and experience and the free exchange of information among contemporaries. Desire simply to get a product has given way to real search for knowledge and the discovery of laws and principles. The solitary lives and the cherished secrets of the alchemists have made way for the free and open world-wide movements and interchange of ideas that have made our times such an age of industry, and to take one example from out of the many, have made it possible for a contemporary, or a follower, to crown with success the efforts of groups of men that have labored to reproduce the precious stones.

Of the precious stones, the diamond, the emerald, the ruby, and the sapphire have all been successfully synthesized. Only the ruby and the sapphire, however, have outgrown the laboratory stage of production, and are fast becoming important members of the field of chemical industry. The less precious stones, amethysts, garnets, tourmalines, etc., have not appealed to the chemists because they are not valuable enough as natural products. The pearl, though a true precious stone, is almost altogether of animal origin. Only the diamond, the emerald, the ruby, and the sapphire will be considered in this paper. It will be helpful to consider the characteristics common to all the precious stones before tracing the development of the production of these stones through their checkered careers.

The precious stones owe their value mostly to the permanence of their beauty. The beauty is due to their intrinsic composition and to the way the stones are made to affect light by being cut in certain forms. The permanence is due to their hardness and to the fact that the stones are chemically inert and resist corrosion. To be sure, extraneous conditions, such as custom and rareness, may affect their value. In the case of the gray diamond of Africa, the bort, and the hardest known diamond, the black diamond of Brazil, the carbonado, we have the only instance of the precious stones being very valuable when not beautiful.

Color, whenever found in the gems, is due to impurities which are usually minute quantities of the metallic oxides. Various colors in the different precious stones can be produced by the same oxide, and the same color in the different precious stones has been traced to different oxides.

The precious stones are transparent crystalline varieties of very common minerals. The diamond may be considered as the chef d'oeuvre of the earth's work on carbon. The ruby and the sapphire are part of the large family, corundum, of which the ordinary emery stone is a very humble relation. Stones identical in composition with the emerald are so common at Limoges that the mineral is said to be used as paving blocks.

Each of the precious stones may be made to lose some or all of its characteristics—its color, crystalline structure, transparency, and even hardness—and be made to return to common clay, so to speak. On the other hand, the "common clay" may be reacted upon in such ways that it may take on all the properties of the precious stones.

Research along the lines of the precious stones has been most profitable when emphasis was placed on experiments that would lay bare the conditions that are necessary to produce the stones rather than on those which would merely bring about products. In the case of the diamond and the emerald these conditions are not known; in the case of the ruby and the sapphire they are so well understood that the making of these has now formed part of the ever-growing field of chemical industry.

THE DIAMOND

The transformation of diamond to graphite or carbon has

been accomplished again and again. The process has also been reversed and some few diamonds have been produced by various investigators. Nevertheless, no interpretation of the phenomena has, as yet, been given. The work of Moissan¹ is extremely interesting, but not enlightening. He obtained his clue from the analytical work of Friedel.²

The Devil's Canyon was once littered with meteorites. Some of these found their way over to France and when analyzed by Friedel tiny diamonds were found imbedded in the mass of



FIG. 1.—ACTUAL OPERATION OF ELECTRIC FURNACE AS USED BY MOISSAN

iron. Moissan tried to reproduce the conditions of the fiery meteor. In an electric furnace he placed a carbon crucible containing pure iron and very pure carbon. The carbon dissolved in the molten iron until a saturated solution was formed, and while the material was at white heat he plunged it in a bath of molten lead or mercury. The sudden cooling caused tremendous internal pressure and the liquid carbon was crystallized into diamonds. The products were microscopic, but were hard, showed the crystalline form, and on chemical test proved to be diamonds. One little fellow weighing about 6 mg., when burned in oxygen produced about 23 mg. of carbon dioxide. Theoretically, 22 mg. should have been produced.

The high dispersion of light—which is twice as great as that of glass—gives to the diamond its so-called "play of fire." In addition to this property the diamond reflects almost all the rays of light that strike its surface and give it the characteristic luster known as adamantine. To these properties, accentuated by the lapidary's art, the diamond owes its beauty. The chemical inertness of the gem has made it possible for the stone to conserve its beauty through the ages. The diamond, most valuable when colorless, is found, however, in very many colors.

THE EMERALD

Chemically, the emerald is a metasilicate of aluminum and glucinum, $\text{Al}_2\text{G}_2(\text{SiO}_3)_2$. Hautefeuille and Perry,³ 1890, dissolved the constituents of the gem in their relative proportions in a bath of dimolybdate of lithium and keeping the bath at 800° C. for fifteen days, succeeded in crystallizing out tiny emerald crystals. A little chromic oxide was used to give the green color. These crystals are in every way perfect, but too small, the largest being only 2 mm. long by 1 mm. wide and 1 mm. thick. They were very expensive, much more so than the earth-made product.

Beyond this successful laboratory attempt, no one has, up to the time of this writing, made public the making of, if made at

¹ See *Compt. rend.*, 1892, 1893, 1894, 1895, 1896 (le four électrique).

² Friedel, "Sur l'existence du diamant dans le fer météorique du Canon Diabolo," *Comptes rendues de l'Académie des Sciences*, **114**, 1037, Dec. 12, 1892.

³ *Annales de chimie et de physique*, 1890, 6 serie, tome XX, pages 447, etc.

all, the emerald on an industrial scale. The experiment of Hautefeuille and Perry, though extremely interesting, is not very instructive, and, as with the diamond, we are not much nearer to knowing what are the conditions necessary to be attained to make the emerald.

The emerald owes its value to its green color and resembles the color of the grass in the spring. The common beryl is a golden yellow. The emerald is identical with it in every respect, save color. This difference is due simply to the presence of different impurities. Almost all the rays of light impinging upon the surface of an emerald enter it, and very few are reflected from its surface, very much as in the case of glass. Furthermore, the emerald is not as optically dense as the diamond. We have, therefore, neither the metallic luster nor the "play of fire" as in the diamond. However, there resides in the emerald a rich, soft, green color that gives to the stone a charm that is to some much more fascinating than the brilliancy of the diamond.

THE RUBY

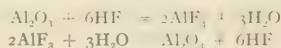
The ruby was the first of the precious stones to be synthesized on a commercial scale and has a more fascinating history than either the emerald or the diamond. Chemically speaking, it is simply the oxide of aluminum with a trace of chromic oxide, to which it owes its rich pigeon-blood color. The natural product has traces of other impurities that play a rôle that seems to us, in our present lack of knowledge, to be far out of proportion to their actual size. The synthetic product is oft-times ruined in the making by quantities of impurities that are so small that they can scarcely be detected by analytical methods. Corundum is often free from the oxide of chromium and we have either a colorless stone, or, if some other oxides are present, we may have a blue stone—the sapphire—or shades of green, yellow, smoky tinges, etc. As an example of the traces of impurities in the natural product, note the effect of radium emanations on some of the earth-made rubies, sapphires, and colorless corundum, and the non-effect of the emanations on the synthetic rubies and colorless corundum. (The effect of radium on the synthetic sapphires has not yet been ascertained.) F. Bordas using radium bromide of 1,800,000 activity turned rubies into brick-red color, white into brown and black, and blue stones into greenish to yellowish tinged stones. The synthetic stones were not affected. These very same transformations have been produced by the writer in the case of some synthetic rubies and colorless corundums by the admixture of a trace of the same impurity in each of the stones. (The influence of this material plays so great a part in the industry that I hope the non-mention of same will be excused.)

Crystalline transparent alumina can be crystallized out of molten baths, can be condensed as crystals from its gaseous state, and can be "frozen" into crystals from the molten state.

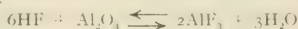
The most interesting attempt to crystallize alumina out of molten baths was that of Frémy and Hautefeuille. The oxides of lead, aluminum, and chromium were fused in a large crucible for about seven to eight days in a furnace used for glass-making. Masses of rubies from 30 to 40 kilos were sometimes obtained, but among these not a ruby was found that was thick enough to be of any value as a gem. One of the crystallographic axes developed more than another, and only thin, laminated crystals were produced.

The attempts to condense the alumina vapor produced similar useless crystals, judged from the view point of gems. About this time we have a new generation interesting itself in the same problem. Frémy worked with a number of collaborators, during 1877-1890. They found that alumina and hydrofluoric acid, on being heated, would cause the aluminum fluoride formed to be reacted upon by the water vapor produced

and condense as corundum. As they were originally written, we have



At that time there was only a suspicion that there were such phenomena as chemical equilibria (writing the previous reaction thus:



the reversibility of the reaction and the existence of the equilibrium is easily noticed).

But the platinum ware to carry out the above was too costly, and Frémy and Feil, and latter Frémy and Verneuil, carried on a series of brilliant experiments with ordinary sand crucibles. It was found that in the presence of vapor of K_2CO_3 amorphous alumina would be changed into corundum. Sand crucibles were filled in the following manner: Alumina, K_2CO_3 , and Cr_2O_3 were mixed with fine charcoal, which was packed around a core composed of alumina and CaF. Upon gently heating, the charcoal escaped as CO_2 and made the mass porous. Each tiny hole became a nest, as it were, where a tiny ruby was born. The slower the process, the larger the rubies that were produced. Carrying on the process in only eight days the largest stone produced was 4 to 5 mm. long and about 1 mm. thick, weighing about one-third carat, or 60 mg. To produce larger stones the process would have to be carried on infinitely slower. If the assumption be correct that a large stone could thus be made, the product would be, of course, very interesting, but the process much too costly.

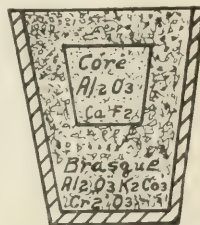


FIG. 11.—ARRANGEMENT OF CRUCIBLE IN THE EXPERIMENTS OF FRÉMY AND HIS COLLABORATORS

Thus the corundum crystallized out of molten baths or condensed from vapors produced only thin, laminal crystals. These not only were too thin to be cut into gems, but lacked the beauty of the earth-made product which appears to be made up of a series of layers. The light coming through these layers enriches itself and gives to the ruby its wealth of color.

Rubies are made to-day by fusing alumina in the oxyhydrogen flame and permitting the molten mass to solidify in the cooler zones of the flame. With the introduction of the oxyhydrogen torch of St. Clair Deville, experiments were begun. Here, again, Gaudin turned his attention to the synthesis of the ruby. He succeeded in fusing quartz which has a melting point slightly higher than corundum with the oxy-hydrogen flame. He tried for thirty years to fuse alumina into corundum but without success. So long as the material was in the flame it was transparent, but the alumina cooled into opaque masses when the flame was removed. Gaudin¹ in his last memoir concluded that it was impossible for him to produce transparent corundum by using only alumina because of the great tendency of the substance to devitrify (become opaque). Moreover, alumina melts at a very high temperature without passing through a pasty state. It suddenly becomes fluid like water and then vaporizes and rapidly disappears like camphor.

Rubies are made to-day by fusing alumina in the oxyhydrogen flame and permitting the molten mass to solidify in the cooler zones of the flame. With the introduction of the oxyhydrogen torch of St. Clair Deville, experiments were begun. Here, again, Gaudin turned his attention to the synthesis of the ruby. He succeeded in fusing quartz which has a melting point slightly higher than corundum with the oxy-hydrogen flame. He tried for thirty years to fuse alumina into corundum but without success. So long as the material was in the flame it was transparent, but the alumina cooled into opaque masses when the flame was removed. Gaudin¹ in his last memoir concluded that it was impossible for him to produce transparent corundum by using only alumina because of the great tendency of the substance to devitrify (become opaque). Moreover, alumina melts at a very high temperature without passing through a pasty state. It suddenly becomes fluid like water and then vaporizes and rapidly disappears like camphor.

The matter was given up for about fifteen years, for there was little hope proffered for its fulfillment. It then happened that rubies appeared on the market whose origin could not be accounted for. It was explained that a mine was discovered near Geneva. As a matter of fact, a curate, or priest, succeeded in fusing chips of natural rubies given him by the lapidaries of Geneva, into large stones. If ruby chips could be fused, then Al_2O_3 could. This latter, Verneuil² succeeded in accomplishing after many years of labor, and developed the process so that

¹ *Compt. rend.*, **69**, 1343.

² *Annales de chimie et de physique*, **8**, serie II (1894).

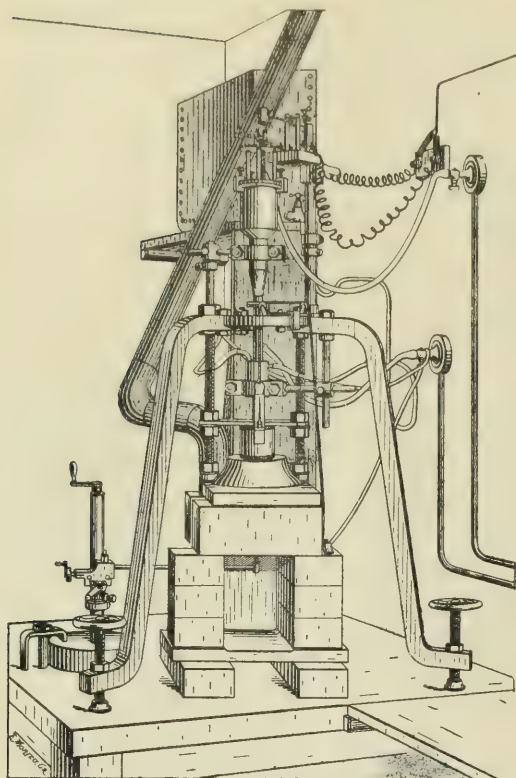


FIG. III—AN EARLY TORCH OF PROF. VERNEUIL FOR THE SYNTHETIC PRODUCTION OF THE RUBY

rubies could be made that were large in size, good in color, and at sufficient speed to make the industry possible.

A modified inverted oxy-hydrogen torch of Deville is used as the starting point in modern practice. It produces a flame

the oxygen, extends about a foot beyond the outer and has a cylindrical shaped top. In the lower portion of the torch, the outer or hydrogen carrying tube extends an inch or two beyond the oxygen tube. The ruby forming powder is placed in a sieve bottom box which, in turn, is screwed into the cylindrical top of the oxygen tube.

When the torch is lit, a little hammer is caused to knock periodically on the top of this box, and particles of alumina are

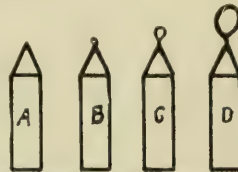


FIG. IV—DIFFERENT PHASES IN THE MAKING OF THE RUBY
A = CONE OF Al_2O_3 SIMPLY FRITTED
B = FORMATION OF PIN HEAD
C = ENLARGED BOULE
D = STILL LARGER BOULE

thus blown into the flame. In the beginning of the process, the flame is comparatively cold and just heats an earthenware rod that is so placed as to catch this powder. As the powder continues to fall on this rod it forms a pyramid of fritted alumina. The heat is gradually increased until the top of this pyramid becomes molten and a tiny stalk, so called pin-head, begins to grow. At this stage the flame is made still hotter and the powder falls in molten drops upon this pin-head. Each succeeding drop falls upon a larger base until an unflawed pear shape, or so-called ruby boule, is produced.

This boule is one single crystal with the optical axes directly perpendicular to one another. When the stem of this boule is broken the stone breaks in two. The great difficulties encountered by Prof. Verneuil in his early attempts were because of this peculiar nature of the stone. Accidentally he obtained a small boule formed on a long, straight stem, and for many years afterward failed to reproduce the same result. The rubies that he tried to make were all formed on a very wide base, and upon cooling broke into tiny particles.

Pure alumina is one essential of this process. The presence of 0.0005 of 1 per cent. of a certain impurity is sufficient to absolutely discolor the ruby, and produce a brick-red instead



FIG. V—MAKING SYNTHETIC STONES AT THE PLANT OF L. HELLER & SON, PARIS

of many zones varying in temperature from 1900° to 2400° C. The torch consists of two concentric tubes: the inner tube carries

of the pigeon-blood stone. In our making of alumina a very interesting state of equilibrium occurs, the ignorance of whose

presence caused a loss for a short time of about 16 per cent of the product. There are many technical details connected with the getting of pure alumina. Suffice it to say that the material must be extremely pure, for every impurity has a tendency to ruin the product by either spoiling the color or making the material brittle. The delicacy of the entire process may be inferred from the above.

The stone cut from a boule is in every way similar to the natural ruby. Physically and chemically these stones are



FIG. VI—VIEW IN PLANT OF L. HELLER & SON

identical. There is perhaps but one method of telling the synthetic from the natural stone, and that is that in the natural stones the imperfections have flat bounding sides and are so-called negative crystals; the imperfections in the synthetic stones have round surfaces and are simply air bubbles which in many cases can be detected only by a powerful magnifying glass. Both the natural and the synthetic stones are made up of a series of successive layers. In the case of the synthetic stone, one can realize from the way it is made, the layers are curved; the natural product has flat parallel layers.

THE SAPPHIRE

It will be remembered that the synthetic ruby industry first started with reconstructed stones. Sapphire chips, however, can not be fused into reconstructed sapphires in a similar way because the color disappears. This phenomenon was excellent material for half-baked interpretations with corresponding results.

We took up the research on the sapphire in our laboratory in Paris in 1909 with Prof. Verneuil as chief chemist.

The sapphire owes its blue color to the presence of minute quantities of the oxides of iron and titanium; however, up to the synthesis of the sapphire, there exists no complete analysis showing both of these oxides to be present in the gem.

The method employed in the research was, in brief, the making of corundum beads or boules by means of Prof. Verneuil's torch and method of fusion, and studying the coloring properties of the various oxides. The research was further correlated with the earth-made product with past experiences in pure and applied chemistry. The view point was necessarily always taken from the only means at hand to produce corundum beads. The history of the gem, such as the duration of time, tem-

perature, and pressure that the earth might have employed, was, of course, an enigma, so that the view point taken to correlate the gem with the products that might be made in the laboratory was that the sapphire was simply an earth-made bead, blue in color, etc. Although the melting point, about 1870° C., and boiling point of corundum are quite close, still, by Verneuil's method of fusion, some phenomena of corundum solutions may be observed and interpreted. In this way the

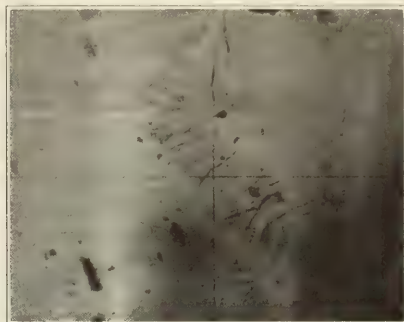


FIG. VII—SAPPHIRE—"RIFTS" OR BREAKS IN BODY OF STONE (125 DIAM.)

research was brought in line with past chemical experiences with the result that many reactions could be predicted. The production of blue articles in ceramics, or other fused products of industry, or the occurrence of blue in the fusion of any of the alumina materials, such as bauxite, or any high temperature reaction which produced bluish colored products, especially those in which the oxides of interest played a part, were carefully investigated. In this way the research was further correlated with past chemical experiences.

Some of the negative results following the various clues were,



FIG. VIII—SAPPHIRE—BAND OF CAVITIES UNDER THREE FACETS (125 DIAM.)

nevertheless, quite interesting, but only a few can be mentioned here. In the majority of cases the clues followed gave positive results. In some of the experiments of Sainte Claire Deville and Carron¹ to obtain the ruby, blue patches were obtained, and it was believed by them that the sapphire owed its blue color to a lower oxide of chromium. Successive experimenters, however, failed to realize any blue color by the use of some of the oxides of chromium. The cobalt oxides, which are used so extensively in ceramics to produce blue, can not, for some reason or other, be retained in the corundum. By the addition of materials such as CaO, blue stones are obtained which are, however, not genuine, synthetic sapphires.

¹ *Compt. rend.*, **66**, 765 (1858).

In Gintl's¹ work on the fusion of bauxite in the electric furnace, some blue patches of corundum were made which showed, on analysis, to consist of TiO_2 , 0.65; FeO , 0.79; MnO , 0.50; CaO , 1.83; MgO , 0.35; NaO , 2.07; SiO_2 , 12.28; Al_2O_3 , 81.88. Scoria in the blast furnaces are sometimes blue, and owe their color to the presence of titanium. Titanium, while not found in abundance in any one locality, must, nevertheless, be widely distributed for there appears to be more titanium than carbon in the earth's crust. The titanium oxides grade away in color from the white of TiO_2 through blue to purple when you get to Ti_2O_3 . Attempts to make lower oxides with hydrogen were not successful. Ferric oxide at 1300°C . to 1350°C . dissociates into Fe_2O_3 , or the lower oxide; and the oxides of iron or pure Fe or any compound of iron become FeO or, perhaps, Fe_3O_4 when fused with corundum. The bead, or boule, is light gray to colorless. Thus iron and titanium when fused with corundum undergo oxidation and reduction. The products that were obtained by this fusion were pinkish. In ordinary solutions, it is well known that every oxidation and reduction is accompanied by change in color. It was this phenomenon that was taking place in the production of the pinkish color. Attempts to get the blue were accompanied with so little success that substances other than iron were used to reduce the titanium. Anatase is blue and has a small percentage of one of the oxides of tin. SnO and SnO_2 with TiO_2 showed very little tendency of reduction. The reaction between iron and titanium is very strongly reversible. By simply adding a slight excess of one of the oxides, the reaction can be made to go in the direction of reduced titanium, resulting in perfectly blue corundum boule. The ultimate production of the sapphire in the laboratory left very few technical problems unexplained. This made it possible for the manufacturing department to take up work within a week after the successful conclusion of the research. Little change has been found possible since.

The corundum boule is in every respect identical with the earth-made product. Experts are much less able to tell the synthetic from the earth-made sapphire, than they are the synthetic ruby from the earth-made ruby.

After fusion only part of the iron and titanium oxides are left. Prof. Moses² found only traces of Fe_2O_3 and about 0.1 of 1 per cent. of TiO_2 . The analysis of the natural products extant before the synthesis of the sapphire did not show the presence of titanium oxide. Prof. Verneuil³ has very carefully analyzed some sapphires from Australia, India and Montana that were perfectly clear under a magnifying glass with the following result in percentages:

SAPPHIRE FROM	AUSTRALIA	INDIA	MONTANA
Iron oxide.....	0.92	0.72	0.56
Titanium.....	0.031	0.04	0.058
Silica.....	a trace		0.10

The unpolished earth-made and the synthetic ruby or sapphire is far from being a thing of beauty. It requires the lapidary's art to bring out their intrinsic qualities. The earth-made products can lend distinction to their wearers and therefore are very highly prized. The synthetic products because of their intrinsic beauty and genuine worth appeal to the many. About 10,000,000 carats of rubies and about 6,000,000 carats of sapphires are produced annually and the demand is growing very rapidly.

LABORATORY OF INTERNATIONAL OXYGEN COMPANY
NEW YORK

THE GOVERNMENTS' INTERESTS IN THE PULP AND PAPER INDUSTRY¹

BY MARTIN L. GRIFFIN

RAW MATERIAL

Book paper is almost wholly made from wood by chemical processes, resulting in recovery of only about half its solid contents in pulp. It takes about two cords of wood for one ton of pulp and the wood alone will cost about twenty dollars. This will average about half the total cost of producing bleached pulp at the present time. How important then is the item of wood!

Economies in the process of manufacture have been possible and necessarily effective, but nothing more can be gotten out of the wood than it contains.

EARLY HISTORY OF PULP-MAKING

In the early days of chemical wood fiber the processes were crude, labor and wood plentiful and cheap. Chemical wood pulp mills were located in such places as Philadelphia, Providence, Derby, Conn., Holyoke (two mills), Turner's Falls. England was a pulp-producing country. These mills went out of business years ago with the receding supply of wood. Ever since, the manufacturers of this pulp have either moved up to the supply or the supply has been brought to the mill, in most cases at a large expense for transportation, or else manufacturers of this grade of paper have altered their plants to manufacture higher grades.

PRESENT ASPECT

During the past twenty-five years the cost of wood, notably spruce, has doubled; other costs have increased, while the price of paper has remained at a very low level. A great industry in wood papers has been developed at a present capital investment of one hundred and twenty million dollars. Our natural resources in wood have been greatly depleted and converted into paper for the people of the United States at a very low price.

Conditions in the manufacture of this class of papers are fast becoming intolerable even with a protective tariff of \$10.00 per ton, due solely to the vanishing point of our wood supply. The cost of transportation by rail to our mills is a great burden on our manufacturers, which Canadian manufacturers do not have to bear. Once our mills received their wood supply by floating it down the rivers. Now these resources are largely gone and our Canadian neighbors occupy this point of vantage.

THE STATE OF MAINE

Maine occupies a peculiar position in this matter. Formerly, well wooded with the most desirable species for lumber and paper and traversed by more large rivers than any other state, whose head waters are great natural reservoirs, its people built up a great industry. It extended its railroads and enlarged its facilities to this end. All of this growth had its source in the natural resources of the state.

GEOGRAPHICAL LOCATION

Maine, situated as it is at the extreme eastern boundary of the United States, larger in extent than all the other New England states combined, is and forever will be at a disadvantage in doing business in our home markets. There is no possible means of offsetting this transportation handicap to our markets and sources of supply. Some other advantages must exist or else development, so slow in the past, will cease altogether and present industries, of which I am writing, must die out. And I say, when the pulp and paper industry of Maine wanes and finally dies, as it inevitably will within the next twenty-five years if matters are allowed to take their present course, there will be no other to take its place. What motive, what

¹ Paper presented before the Maine Section of the American Chemical Society, Auburn, March 19, 1913.

¹ Gintl, *Zeitschrift für angewandte Chemie*, **1901**, p. 1173.

² *American Journal of Science*, **30**, 4th series, Oct., 1910.

³ *Compt. rend.*, **151**, 1065, Dec. 5, 1910.

incentive, or what object is there to encourage manufacturers to come to Maine? Transportation must be had, it is handicapped; coal must be had, it is costly; of natural resources in minerals, they are very limited; of power there is at present a surplus and an abundant opportunity for development, but at present prices it offers little inducement, and power without customers for it has no value. It is idle to talk about conservation of water powers, with no market to take it, and do nothing but talk about conserving the only means by which such power may possess great and lasting value.

WHAT MAINE IS BEST FITTED TO DO

Aside from its possibilities in agriculture and minor resources, its great potential natural wealth is in its great rivers, lakes and power therefrom and woodlands. Its one great industry is the pulp and paper business. They are wonderfully adapted to each other and either will languish without the other. Rational harvesting and conservation of our present supply, and reforestation, along our great water courses, at the earliest date, will alone preserve this great industry to the state and nation. By so doing the most beneficial results will follow to our people. The wooded areas will conserve the tributary sources of our rivers, make permanent our power from them, and in time the rivers will bear the forest products to our mills at trifling cost.

HOW THIS MAY BE ACCOMPLISHED

The growth of forest woods is very slow, so slow that one generation cannot hope to profit from its own initial investment in tree planting. It is not an annual growth. There is, therefore, no incentive for the individual to plant forest trees, and there is little for the average corporation. The natural resources of our state and nation, in forest and stream, represent a large unearned increment of wealth, which does not rightfully belong to anybody; it belongs to all. Unlike the vast unearned increment of land values in our great cities, in the hands of a few, which should be equalized with society which created it, these values in virgin woodlands have been distributed to all our people with a lavish hand, through the paper mill and press. Great as has been the value of the discovery of printing and the printing press, they would have had no value without paper. Point if you will to the large capital invested in this industry; it has been made necessary by the demands upon it. Unlike the business of banking, speculating, mining and smelting and many protected industries, it includes no millionaires. The unearned increment has gone to the people.

If our state and nation would desire to preserve this business to itself, it must coöperate to conserve what we have left and proceed at once to a practical plan of reforestation, and the regulation of the harvesting of wood. In this I would include all useful woods, and those from which useful products are obtained.

Unless we do this, we may, for a time, obtain the balance of our increasing needs, from foreign sources, at possibly some concession in price. We know, however, that as soon as we cease to be a competitor, we will no longer pay competitive prices. The results of this policy would be the loss of our natural resources, the depreciation of our water powers, the ruin of the larger part of a great industry; the profits of labor, the source of all acquired wealth; and the final increased cost of this commodity in the near future.

WHO OUR COMPETITORS ARE

Germany and Scandinavia with their rational system in forestry will always probably have a surplus, and in any case will necessarily sell in the highest market. At present and for some time to come, Canada will be the chief menace to this industry in our own country. A few years ago Canada's acquired resources were limited; her natural, very great. Development in processing pulp and paper has been largely done by us. Our architects have planned Canada's great mills and our machinery

builders are furnishing a large part of the equipment. We are pioneers everywhere in building and equipping the largest and fastest running paper machine in the world.

It results, therefore, that Canada has to-day all we possess and large resources in wood which we no longer have. The larger part of our wood now comes from Canada and it requires skilful diplomacy to get it.

SUBSTITUTES FOR WOOD

There is a popular view, which has been erroneously fostered by our government, that there are exhaustless resources of waste fiber in our country, suitable for paper, and a substitute for wood. I once thought so myself. It is very natural to think that the discarded stalks of sugar cane, corn, cotton, rice, flax and other plants, which mature annually, would prove an abundant substitute for wood. These have all been exploited for twenty-five years to my personal knowledge with no visible results. A plant has one main function to perform—it is to flower, fruit or make stalk. Its other functions are subordinate and produce only by-products. No by-products can be substituted for the main product. The stalk is the main product of the forest tree. No other raw fibrous material is so rich in cellulose; no other lends itself so easily to paper mill processing. It has no seasons of harvest, does not require curing, does not easily decay, requires no packing and may be stored best in the rivers. All these waste stalks are pithy, bulky and perishable and would require much labor to gather, pack and ship. These are but a few reasons why we may expect no practical results from this source. Wood fills a place no other material can. There is no substitute for it.

WHAT THE GOVERNMENT SHOULD DO

First, it should protect this industry not because we pay our laboring classes more—this is now a worn-out argument and the difference is not worth talking about—nor because there is a trifling duty upon a few chemicals we do not import. There is a duty of \$2.50 per ton on china clay which should be free, as it does not exist in our country, but this is not a burden. The paramount reason why this great industry should be protected is because the vanishing point of our raw material in wood is coming nearer every year. Given its raw material on equal terms with other countries, it needs no protection. This protection should be equal to the difference in the cost of wood laid down at the mills. It would be better to make it more than this and to use the entire revenue so derived in the work of reforestation.

Second, the state should protect its visible supply by putting a tax upon all timber cut at so much per thousand feet as a renewal and depreciation fund, to be used coöperatively, by which I mean to include all who cut timber for profit. There should be coöperation and joint responsibility to give back to the soil, for the benefit of those who come after us, their share of the unearned increment in timber values we have not earned.

I advocate, therefore, the levying of a duty by the federal government upon all imports of wood products, either as paper or to be used in the manufacture of paper, equivalent to \$5.00 per cord of 128 cu. ft., and that the revenue, therefrom, be devoted to reforestation under a rational scheme of distribution and control.

This equivalent would amount to:

- \$ 5.00 per ton on mechanical ground wood.
- \$ 6.25 per ton on common news.
- \$10.00 per ton on chemical wood pulps.
- \$10.00 per ton on chemical wood papers.

Also the levying of a tax by the several states on all timber cut for profit, the proceeds of which to be devoted to conservation and reforestation within their own boundaries.

The wood pulp paper industry once thriving in New England, Pennsylvania, New York, Ohio, Michigan and Wisconsin, is

now flitting about the international boundary and will soon vanish to the other side unless heroic means are taken speedily to preserve this industry to our home market, the greatest in the world.

RUMFORD FALLS, MAINE

THE TRAINING OF THE FERMENTOLOGIST¹

By CARL A. NOWAK

Received March 14, 1913

The fermentation industries are constantly in need of university-trained men. These are difficult to obtain. It appears that at present there is no university in the United States which has outlined courses of work suited to the requirements of students wishing to enter the fermentation industries, not as brewery managers or brewmasters, but in the capacity of technical experts, chemists, chemical superintendents, or as instructors and chemists at the recognized technical colleges or brewing institutes.

These brewing institutes, which are usually maintained in connection with technical laboratories, also known as scientific stations for brewing, require men capable of undertaking, besides teaching, also analytical and research work pertaining to the fermentation industries. Some of the breweries and malthouses have, to some extent in advance of the viticultural establishments, learned to appreciate the value of scientific control; they possess their own laboratories, and they need chemists and chemical superintendents.

The scientific stations for brewing are the result of a more or less general demand on the part of the entire brewing industry for laboratory control of the different brewing operations. Such outside control becomes especially important and valuable when the establishment of a private laboratory in a brewery does not appear feasible, owing to the large expense of installation and still greater cost of maintenance. Membership in these stations is established on the payment of a certain sum a year, in consideration of which the station undertakes to assist the member in controlling the working conditions by frequent tests, analyses and reports covering the raw materials and products.

The analytical work required of these institutes covers water, coal, mineral, general inorganic and food analysis, and general biological work, but is more particularly concerned with such examinations as the analysis and valuation of barley, malt, malt adjuncts, sugars, coloring syrups, hops, and similar raw materials used in brewing with which the average college graduate is practically entirely unacquainted.

From this it follows that the future fermentologist is in need of at least some specialized training, especially if he is also called upon to lecture in the technical school in which the practical brewer or manager seeks to acquire a certain amount of scientific training in order to better fit him for a position of responsibility.

The intellectual development and education of the students applying for membership in these courses is of an extremely varied nature, some possessing good high school, occasionally even college education while others, and unfortunately the majority, are so deficient as to lack even the rudiments of mathematics. All ages from 18 to 60 are represented.

To instruct a class of such varied intellectual ability and to present in the short period of six months (the duration of the course) in a clear and lucid manner all the subject matter outlined, only falls short of a Herculean task. Unless this work is entrusted to a conscientious instructor of more than the average college training, preferably one who is also a student of the human mind, the result is bound to spell failure.

The greatest difficulties are encountered in the teaching of physics and chemistry which are the fundamentals of much of

the other work of the brewing student. Few college men have specialized in biochemistry of plant life, which in the case of the brewing student must receive first attention even to the exclusion of some of the most necessary principles of general chemistry. The commonly accepted method of presenting the subject of chemistry is, due to lack of time, entirely out of the question. It appears not only desirable but in some cases it is absolutely essential that organic chemistry be presented before inorganic, and that the chemical laws and theories, if presented at all, be briefly outlined at the end rather than at the beginning of the course. The labor involved in teaching this subject is furthermore materially increased through the lack of any suitable text-book. It has been my experience, especially in dealing with the older men whose minds are far from being easily susceptible to impression, that the graphic method of presentation, wherever applicable, gives the best results.

These brief remarks, I trust, will show conclusively that the task assumed by the fermentologist is not an easy one, and, furthermore, that to enable him to do full justice to his work specialized training would be an invaluable asset. It may be proper to seek to determine next, what prospects the fermentation industries offer to those specializing in them.

Owing to the lack, at the present time, of any school in the United States in which the young fermentologist can acquire specialized training, it is usually necessary for the brewing institutes to educate their own instructors and chemists while paying them a reasonable salary.

A chemist just graduating from college, and with but little experience, who is expected to teach from 2 to 4 hours a day in the brewery school and to devote the balance of his time to laboratory work either of an analytical or research nature, may demand a salary of at least \$75.00 per month, usually more, ranging anywhere from \$75.00 to \$125.00 per month; that is, it will be conceded a fine salary for a young chemist just starting in business and is also considerably higher than offered in other industries for laboratory or research work. If a man chooses to remain in this line of work, he may eventually receive a good salary. He can also later accept a position at a brewery or malthouse as chemist or chemical superintendent with the possibility of a still greater compensation if he shows capability along technical lines.

For the young chemist, even though he may not intend to remain in the fermentation industries permanently, the experience gathered may become a valuable asset in his later career provided, of course, that he chooses to enter some other organic line of chemical endeavor.

Unfortunately, and unjustly so because there is no sound reason for it, there are men in some of the other industries who consider the fermentologist as inferior to themselves in education and training, possibly based on the erroneous belief that he knows little else than the chemistry of beer. As a matter of fact a man who has been in the fermentation industries for some time has acquired a good chemical training. He must, of necessity, be a good organic chemist, with considerable knowledge along physiological, bio- and colloidal chemistry, branches of the science which play an equally important part in glue and leather manufacture. He has, usually, a good understanding of the correlation of the practical and theoretical work along these lines which offer unlimited possibilities for original work and research of a practical as well as theoretical nature. We only need recall the many intellectual achievements both in chemical and biological science which have resulted from the stimulus to find the meaning of certain of the more important phenomena connected with the science of brewing.

Whether the outlook for the future and the prospects offered the fermentologist warrant the establishment at any of our universities of courses in fermentation is another question.

¹ Paper presented at the Annual Meeting of the American Chemical Society, Milwaukee, March, 1913.

If so, the character of these courses and the time that should be devoted to them remains to be decided upon.

Abroad, especially on the continent, young men wishing to specialize in any particular industry, fermentation included, usually attend, after completion of the customary high school work or "gymnasium," the so-called "technical" high schools, and there receive excellent training.

In England the University of Birmingham maintains a College for Malting and Brewing and a Department of the Biology and Chemistry of Fermentation. As this college is the only one of its kind and offers a most complete course in brewing science, it may be worth while to go at some length into the nature of the curriculum.

Four courses of instruction are provided, which are:

1. A Degree Course in the Biology and Chemistry of Fermentation.
2. A Diploma Course providing instruction on the principles of all subjects connected with Malting and Brewing, and the fermentation industries generally.
3. Certificate Courses for Brewers and for Maltsters who are unable to devote the time to study required for the Diploma Course.
4. Shorter courses of lectures and practical work in the principles of Malting and Brewing.

As regards the two last-named courses these are offered by the brewing schools of this country and need no further comment. The Degree Course is suitable for such students as contemplate taking up biological work in connection with the fermentation industries and agriculture, and bacteriology in connection with water supply and the treatment of sewage, etc. This course is also intended for students who contemplate qualifying for brewers' chemists. After taking the degree at the end of their third year of study, arrangements are made by which such students can take an advanced course of study in the Department of Brewing in their fourth year, following on which the Diploma in Brewing is granted. The Degree Course is also suitable for students who are candidates for the Associateship of the Institute of Chemistry in the Branch of Biological Chemistry.

The Diploma Course is established for students not taking the Degree Course, who wish to obtain a thorough training in the principles of malting, brewing, and the kindred fermentation industries.

No attempt is made to teach practical brewing, the work being confined to the teaching of the underlying principles as thoroughly as possible, the practice work in the laboratory during which the student does and sees things for himself forming the most important part of the training.

Professor Adrian J. Brown, Director of the School, informs me that the difficulties and expense of running an experimental

brewery for students on a scale sufficient to be of practical value, are at present insuperable in England, and anything of the nature of a toy plant is regarded by the faculty as misleading and so worse than useless.

It is expected, however, that every Diploma student will have obtained at least four weeks' experience in a brewery during one of the university vacations, before he commences his third year's work.

The studies arranged for the first and second years of the Diploma Course are, with the exception of brewing technology, not technical, but are carried on under the Professors of the subjects with the intention of thoroughly grounding the students in the principles of the various sciences concerned, so that they may be prepared to take full advantage of the training in the brewing department in the third year, and be able to grasp thoroughly the scientific problems involved in the technology of the fermentation industries.

I do not think it likely that conditions in this country will ever be such as to enable any of our universities to found a brewing college on the plan of The British School of Malting and Brewing of the University of Birmingham. I believe, however, that one of our universities, which like the University of California possess not only an excellent biological and physiological department but also conduct courses in vinification and zymology, could easily outline a special course for brewing students. Possessing as it does excellent facilities, in the form of zymotechnical and viticultural laboratories, very little additional apparatus would be required to meet all the requirements of the brewing student. Lecturers from other departments could be drawn upon to a large extent, and if circumstances would warrant it, possibly one Professorship in Brewing and Malting could be established. I have no doubt but that some of the progressive men interested in the welfare of the brewing industry would be quite willing to contribute to the maintenance of such a department or professorship, and possibly also to a fund for the founding of a Department of Preventative Medicine, to study in particular the nature and physiological action of alcohol.

For the present the best plan for some of our universities to carry out would be to offer a post-graduate course in brewing, possibly of six months' duration, to which only such men would be admitted as already hold the Bachelor Degree in Science. On the completion of this course a diploma in Biology and Chemistry of Fermentation as applied to brewing could be granted. There is little doubt but that such a step would mean a great advance in brewing science and would greatly benefit not only the student but also indirectly the university, and finally the brewing industry-at-large.

WAHL-HENIUS INSTITUTE OF FERMENTOLOGY
CHICAGO

WILLARD GIBBS MEDAL AWARD

The Willard Gibbs Medal for 1913 was presented to Doctor Leo H. Baekeland, at a special meeting of the Chicago Section of the American Chemical Society, held in the Sherman Hotel on May 16th. The award took place in the Louis XVI Room and was preceded by a reception to Dr. Baekeland from six to seven o'clock. In addition to Dr. Baekeland there were in the reception line Prof. Stieglitz, Chairman of the Chicago Section; W. D. Richardson, who was to present the medal; William A. Converse, donor of the medal; Prof. Edward Bartow, of the University of Illinois; Prof. George B. Frankforter, of the University of Minnesota; Prof. Neff, of the University of Chicago; William Brady, of the Illinois Steel Works; Prof. Harry McCormack, of Armour Institute; Prof. W. R. Smith, of Lewis Institute; and Dean James R. Angell, of the University of Chicago.

The reception was followed by a banquet attended by nearly two hundred Chicago chemists and a large number of ladies. Prof. Stieglitz presided at the formal meeting. Mr. Richardson made the presentation address in connection with which he followed very carefully the achievements of Dr. Baekeland from a period many years before the discovery of Velox paper, up to the present time.

Dr. Baekeland on receipt of the medal was for several moments rather at a loss for words, but deeply felt the honor in having his name connected with those of Arrhenius and Richards, the earlier recipients of the medal, and Willard Gibbs for whom the medal is named. After Dr. Baekeland's address, Dean Angell, of the University of Chicago, spoke upon some of the possibilities of Dr. Baekeland's work and upon the general attitude of the University toward the technical chemists. This

was followed by a short talk from Dean George B. Frankforter, of the University of Minnesota, after which the meeting stood adjourned.

The Chairman's address, the presentation address and the address of acceptance by Dr. Baekeland are herewith published in full. [EDITOR.]

CHAIRMAN'S ADDRESS

By JULIUS STIEGLITZ

LADIES AND GENTLEMEN:

Perhaps the most significant feature of our gathering here this evening to witness the bestowal of the Third Willard Gibbs Medal upon our honored guest lies in the fact that for the first time in the history of the medal it is to be bestowed upon an eminent investigator in the field of *applied* chemistry. Svante Arrhenius and Theodore W. Richards, our first two medalists, were among the highest in the ranks of what for want of a better name we are wont to call "pure chemists." Willard Gibbs himself was *simon pure*—in his best days he did not soil his hands even with the grime of a laboratory, with nitric acid, permanganate or anilin dyes, and he did not carry home with him any of the lurking odors of the laboratory at which every good *hausfrau* turns up her little nose—no trace of hydrogen sulfide, phenyl isocyanide or carbon disulfide could linger in his beard and be commented on when he reached home—for Gibbs' great work was done in his study, developing the great mathematical generalizations of thermodynamics underlying all of chemistry. No doubt, if he had been summoned by some anxious would-be client, a great manufacturer, perhaps a trustee of Yale University, he would have had exactly the same experience that Dr. Jones, Doctor of Philosophy and Professor at the University of Michigan, tells on himself. One day the telephone at his house rang vigorously; his housekeeper answered it and Dr. Jones overheard the following dialogue: "Is Dr. Jones in?" "Yes, he is." "Then tell him to hurry right over to X and Y street to help a boy that has hurt himself very badly." "Oh," replied the housekeeper, "Dr. Jones is not that kind of a doctor." But the party persisted. "What's that? He should come right over, we need him at once"—and the housekeeper peevish and unable to explain that a doctor of philosophy is not a doctor of medicine, replied rather too emphatically, Prof. Jones thought, "*You don't want him—he is the kind of a doctor who has never done any one any good.*" I am very much afraid that is the kind of comment an average man, perhaps even among chemists, is inclined to make about

"pure chemists"—in fact, I know it is so from a recent correspondence with a gentleman in Salt Lake City intensely interested in a shoe polish. Dean Angell sent us a request from this gentleman for the analysis of a sample of shoe-blackening, which all the analytical chemists of Salt Lake City had been unable to manage—so he sent it to the chemists of "the great University of Chicago." Professor McCoy replied briefly that we do not accept commercial work. A prompt reply came from our friend: "I am sure that if I slipped a fiver into the hands of Professor Stieglitz or Professor McCoy, they would come down out of the clouds and jump at the chance—of what good is their star-gazing anyhow"—or other words to the same effect.

I need not remind this distinguished gathering that after all the work of Willard Gibbs in pure chemistry was of the greatest

good to the greatest number—work that can draw from an Ostwald the words "He has given form and content to chemistry for a hundred years" has surely done this good. But if Gibbs were here to-day, he would be the first to endorse the wisdom of the wish of the founder of our medal, Mr. William A. Converse, and the wisdom of the provision of this Section, which has accepted the honor and duty of awarding the medal, that the Willard Gibbs Medal shall be bestowed annually on some chemist who has been preëminent in research and that advisedly no distinction as to the field of work, whether in pure or in applied chemistry, was made. If time permitted I could dilate on the fact that both fields of labor have as ultimate fruits results of highest practical importance as well as of highest theoretical value. We owe the contact process of manufacturing sulfuric acid, we owe the recent methods of securing inexhaustible supplies of fertilizers, ammonium salts and nitrates, from the atmosphere, to the work of chemists applying the processes of reasoning of theoretical chemistry—and on the other hand, we owe the theory of color and dyes in organic compounds to a technical chemist, Otto N. Witt, and many of the fundamental theories of organic chemistry of to-day grew out of Baeyer's work on the synthesis of indigo. It is altogether fitting then, in view of the common results in all branches of chemistry, that the Chicago Section of the American Chemical Society should bestow its medal, named after the greatest chemist America has developed, on great investigators in all the varied fields of chemistry—they all contribute to the happiness and welfare of the human race. We are fortunate indeed that so early in the history of the medal we are able to bestow it on a chemist who has enriched, not one, but a number of branches of service with the work of his genial brain. I shall leave it



DR. L. H. BAEKELAND
WILLARD GIBBS MEDALIST, 1913

to Mr. Richardson to tell you a little of all that Dr. Baekeland has done—Mr. Richardson has himself given heed in the field of applied chemistry to the insistent demand for original thinking, the prying out of Nature's secrets by scientific endeavor. I shall close my remarks by referring only to the one fact, that through his invention of Velox photographic paper, Dr. Baekeland not only opened up an entirely new and great field in photography but has enriched tens of thousands of lives. Dr. Baekeland has gone so far beyond Velox that he claims to have forgotten all about it, by now, but no doubt Mr. Richardson will give us an up-to-date, as truly complete and artistic a picture of Dr. Baekeland's services to chemistry, as Dr. Baekeland's Velox gives Mr. Richardson faithful and artistic reproductions of his own beautiful work with the camera.

PRESENTATION ADDRESS

By W. D. RICHARDSON

DR. BAEKELAND, MR. CHAIRMAN, LADIES AND GENTLEMEN:

We have gathered here to-night in recognition of the services of one who has materially aided human progress, and in adding to the sum of knowledge has increased the sum of human happiness. To emphasize or memorialize this recognition, we are to present our guest of honor with a medal, founded by Mr. Converse, and named in honor of Willard Gibbs, who although known as a mathematical physicist was, in fact, one of our most illustrious chemists.

The man who accepts a medal takes upon himself a heavy responsibility. Like the man in the story he places himself in the hands of his friends in a most absolute way. There is no relief or rest for him from the time he arrives in town until he is safely aboard a train and on his way home. There is every likelihood of his being overentertained and overfeasted. But worst of all, people inquire what he has done to merit the award and look up his record as though he were a politician of another party. And by accepting the medal and placing himself at the mercy of his friends he may even have to sit patiently and listen to a recital of some or all of his scientific labors and results and appear to be at ease. Dr. Baekeland, I hope you will be able to bear the worst that is to come with fortitude and a smile. Where the record is clear, where the work has been well done and permanently done, there should be no embarrassment to the doer in the admiration of his friends. In such work a man may most properly show his pride without fear of the charge of egotism.

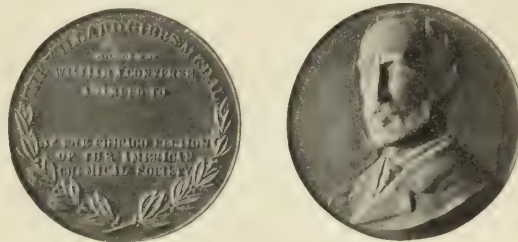
The needs of the world increase with the age of the world. It was not long ago that people got along very well without railroads and steamships, automobiles and airships, not long ago that they got along without tungsten, arc, carbon filament and mercury vapor lamps; without gaslight and kerosene light—indeed, it was only one hundred years ago that there was no stearic acid candle! and the animal and vegetable fats and oils were used for illumination. The chemical inventor of to-day fills a new want as often as he does an old one. Or he may even create a want where there was none before.

Following after the time when he was student and professor in Belgium, Dr. Baekeland came to this country. His first inventions were in the field of the chemistry of light. Prior to 1893 the photographic paper in common use was of the kind known as printing out paper—the kind that requires sunlight and much watching to produce results—even if no mention is made of the after-treatment known as "toning." The results with these papers were good in some respects, full of detail and gradation but the labor involved was enormous. Dr. Baekeland, by his invention of the developing-out paper or gaslight paper, revolutionized photographic print-making. "Velox" was the very felicitous name applied to the invention—the same Velox made by the Eastman Co. to-day and known to all photographers. From 1893 to 1899, Velox paper was

manufactured by the Nepera Chemical Co. under Dr. Baekeland's direction, when the Eastman Co. purchased control. It was the forerunner of all the gaslight papers which are in universal use to-day.

His next work was in the field of electrochemistry, and consisted in perfecting the Townsend cell for the manufacture of electrolytic alkali and chlorine. Under the Hooker Electrochemical Co. the cell was put into practical operation at Niagara Falls. At the present time 34 tons of caustic soda are manufactured daily in this plant and within a year the capacity is to be increased to 64 tons per day. Recently the Farbenfabriken of Elberfeld has adopted the Townsend cell in its works.

His last, and as he looks upon it, his most important work was in the field of organic chemistry, and consisted in the invention and manufacture of condensation products of phenol and formaldehyde. On this subject Dr. Baekeland will speak to us to-night. This work occupied his attention for several years and the scientific work alone connected with it is even at the present time engaging the attention of seven chemists in this country, and, indeed, many chemists in all parts of the world. His patents, some fifteen or twenty in number, and his publications on the subject were issued in 1909 and succeeding years. At present the product, "Bakelite," a substance of most interesting properties as you can see by these exhibits, is worked up in twenty-four different industries. In the button industry alone about 1,000 workmen are employed on the product.



THE WILLARD GIBBS MEDAL

But if I were asked to sum up in a few words the genius of Dr. Baekeland I should say that it is comprised in his ability to follow an idea to its conclusion. In the case of each of his discoveries he has not been satisfied with the mere discovery, however important it was; but in every instance he has carried his work to a practical conclusion—from the laboratory to the factory and from the factory to the public. Let us see what this entails: In the first place a man must have faith in his idea; not only that but faith in himself. Then he must have the scientific knowledge and technical skill necessary to carry his discovery through the laboratory stages and to the small manufacturing stage. Following this the larger factory must be built and started in operation. In the meantime, if the inventor's future rights are to be protected, the inventions must be carried through the Patent Office—a matter of no small importance, and requiring no small amount of information. Then the company must be organized and capitalized and directed. Finally, if the inventor is to be completely successful, he must be a good publicist in order to bring his discoveries before the great consuming public. In all these departments of activity Dr. Baekeland stands preëminent.

And now, having exposed thus briefly the splendid record of our guest, in this barefaced fashion, before him and you—an ordeal which he has borne with the utmost fortitude—I have only the duty left of presenting the Willard Gibbs Medal.

DR. BAEKELAND:

This medal can add nothing to your achievements. Your work and your inventions have already received their merited

recognition by your scientific colleagues and by the world of practical affairs. But in presenting you with this medal the Chicago Section of the American Chemical Society not only desires to give recognition to your discoveries in a very special way but more than that to link your name with those of the famous men who have preceded you—Arrhenius, Richards, and the one after whom the medal is named, Willard Gibbs, as well as with many more who will follow you in after years.

In the name of the Chicago Section and the founder, Mr. Converse, I now present to you the third Willard Gibbs Medal.

ADDRESS OF ACCEPTANCE

THE CHEMICAL CONSTITUTION OF RESINOUS PHENOLIC CONDENSATION PRODUCTS¹

By L. H. BAERLEND

The preparation and utilization of some of the phenolic condensation products, of which I intend to speak, has been repeatedly described in several special publications dealing with this subject, as well as in the patent literature [see Baerlend, *THIS JOURNAL*, 1, No. 3, 149 (1909); 1, No. 8, 545 (1909); 3, No. 12, 932 (1911); 4, No. 10, 737 (1912); *Trans. Am. Electrochem. Soc.*, 15, 593 (1909); Raschig, *Z. angew. Chem.*, 25, 1945 (1912); Lebach, *Z. für angew. Chem.*, 22, 1598 (1909); Lebach, *J. Soc. Chem. Ind.*, —, (1913)].

Many of you are acquainted with these publications. For those who are not, I shall take the liberty to state briefly that these phenolic condensation products, which have of late acquired such importance, are obtained by the action of phenol or carboic acid on formaldehyde under suitable conditions. Instead of formaldehyde, any suitable equivalents of the latter may be used; for instance, hexamethylenetetramine, which is a product resulting whenever formaldehyde and ammonia are brought together.

Whoever is not acquainted with organic chemical reactions may be somewhat astonished to learn that two very ill-smelling liquids, like carboic acid and formaldehyde, should be capable, by an act of chemical synthesis, to engender an absolutely different substance which is solid, hard and infusible, insoluble in all known solvents, resists most chemicals, and which from its external appearance might be mistaken for the most beautiful amber, or for the highest quality of Chinese or Japanese lacquer. If it differs at all from any of the latter products of nature, it is mainly by its superior strength and higher resistive qualities, and by its incomparably lower cost of production.

To those of you also who are still unfamiliar with this substance, it may help your imagination, when it comes to conceive the possible uses thereof, to examine the rather varied exhibit displayed here to-night, of the many articles which have been made by means of these infusible phenolic condensation products. You will notice that these applications vary from cigar holders to switchboards for battleships; from grindstones to self-lubricating bearings; from the most effeminate jewelry, to acid pump valves; from brass-bedstead lacquer, to phonograph records; from billiard balls to automobile magnetos; from unbreakable dolls, to electrical machinery; from buttons to newspaper stereotyping matrices.

I may add that since I made my first publication on this subject, a number of important and prosperous new industries have been brought into life, and an ever-increasing number of new applications are looming up as fast as the technique of this material is being mastered by a larger number of skilled men.

To get as far as we are now, has been by no means easy work, and even now, much had to be left undone or half finished. Only those who ever have undertaken pioneer work can conceive what all this involves, especially when a subject of such a wide range of applications has to be handled, and when those skilled in the art are few and have first to be patiently trained.

In my eagerness to go ahead, progress seemed rather too

slow to me at first, but now that I am beginning to see everywhere the practical results in many different directions, I am reminded of the fact that, after all, it is only a short time ago that the systematic commercial manufacture of the raw products was started. Since then, several factories here and abroad are supplying the raw material in many grades to the numerous industries which have learned to utilize it for the most varied purposes.

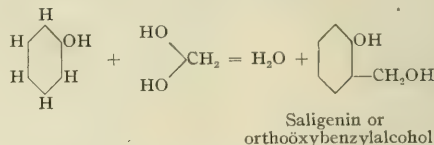
In the meantime, dozens of highly trained chemists and engineers, in Europe as well as here, are spending their daily efforts in the study of further improvements in this new branch of chemical industry, and on the applications dependent thereon. Up till now this country has kept the lead in this industry, although in some European countries, too, much good work has been performed.

While the practical work has been going on steadily, the problem of the purely theoretical side has not been neglected; I now want to devote this opportunity to present this part of the subject. Unfortunately, the study of the chemical reactions involved in these processes is certainly not an easy one. Any organic chemist knows that bodies of a resinous or colloidal nature, which neither crystallize, nor melt, nor distill, nor dissolve, do not belong to the class of substances easy to purify nor to be studied with some hope of accuracy, approaching even in the most remote way what can be accomplished with clearly crystalline or volatile substances.

Neither will chemists be very astonished if such men like Adolf von Bayer, or his pupils, when as far back as 1872 (*Ber.*, 5, 25, 280, 1094, 1095; 19, 3004, 3009; 25, 3477; 27, 2411) they took up the study of condensation products of aldehydes with phenols, were not much attracted by some of the resinous substances which now and then were formed in these reactions, and preferred to devote their attention to the crystalline, well-defined bodies which could be studied with incomparably surer and easier methods.

The same happened with Kleeberg, who in 1891 (*Ann.*, 263, 283), in further work on condensation products, encountered a hard, untreatable substance of which the further study was abandoned in favor of some crystalline condensation products.

I should remind you of the fact that by conducting the action of formaldehyde on phenol under suitable conditions [Lederer, *J. prakt. Chem.*, [2] 50, 224; Manasse, *Ber.*, 1894, 2409-2411; U. S. Pat., Manasse, 526,786, 1894; D. R. P., Bayer, 85,588] a very clean-cut reaction takes place, giving the simplest phenolic condensation product, oxybenzylalcohol or saligenin. In this case, formaldehyde reacts as methyleneglycol:



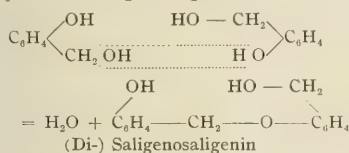
In this same reaction, more or less large amounts of para-oxybenzylalcohol are formed at the same time. But saligenin or oxybenzylalcohol is very easily disturbed by dehydration, and then changes into a resinous mass. This dehydration can occur by simple application of heat, and is much hastened by the presence of strong acids or other chemical agents. This is the reason why in the processes of the preparation of oxybenzylalcohol, low temperatures and general careful treatment are essential. For this purpose, the phenol is first changed to phenolate by the introduction of one molecule of alkali hydrate; the reaction is carried out at moderate temperatures, and afterwards, the oxybenzylalcohol is set free by the judicious addition of weak acids and by extraction by means of fractional solvents.

Unless such careful precautions be observed, the reaction gets

beyond control, and resinous bodies are sure to be produced in predominant quantity. This is especially the case when strong acids are used as condensing agents; but even under such conditions we have succeeded, in my laboratory, in establishing the presence of noticeable quantities of oxybenzylalcohol [Backeland, *THIS JOURNAL*, **4**, No. 10 (1912)]. However, continued application of heat, or the presence of strong acids, or other condensing agents, will soon cause resinification of any of the above-mentioned phenol alcohols, so that in the process of preparation of phenol alcohols, the conditions of procedure and necessary precautions are widely different from those required in the production of synthetic resins.

The resinous dehydration products, derived from phenol alcohols, are known and have been described long ago as saliretin products [Beilstein, *Org. Chem.*, **2**, 1109 (1896); R. Piria, *Ann. Chem.*, **48**, 75; **56**, 37; **81**, 245; **96**, 357; Moitessier, *Jahresbericht*, 1886, 676; K. Kraut, *Ann. Chem.*, **156**, 123; Gerhardt, *Ann. chim. phys.*, [3] **7**, 215; F. Beilstein and F. Seelheim, *Ann. Chem.*, **117**, 83; C. Schotten, *Ber.*, 1878, 784].

Some have proposed a chemical structural formula for these products. For instance, it has been assumed that the first dehydration product disaligenosaligenin is formed as follows:



In the same way, a trisaligenosaligenin, $\text{C}_{18}\text{H}_{16}\text{O}_5$, or $4\text{C}_6\text{H}_5\text{O}_2 \cdot 3\text{H}_2\text{O}$ (K. Kraut, *loc. cit.*; Gerhardt, *loc. cit.*), and a heptasaligenosaligenin, $\text{C}_{48}\text{H}_{40}\text{O}_9$ or $8\text{C}_6\text{H}_5\text{O}_2 \cdot 7\text{H}_2\text{O}$ (F. Beilstein and Seelheim, *loc. cit.*), are formed.

However attractive all such formulae may appear to enthusiastic novices in organic chemistry, the sobering fact remains that every one of above-mentioned substances is of a highly resinous nature. Their very name, "saliretin," has a Greek root which refers to their resinous properties. Whether their constitution is as simple as is indicated by the above formula, is a mere matter of conjecture and entirely impossible to prove by any of the scientific methods available at present. Quite to the contrary, it is more probable that these substances not only have a considerably more complicated molecular structure, but that they are mixtures of several colloidal bodies which exist here together in solid solution. Furthermore, the phenomenon of dehydration may be accompanied by rearrangement of the molecules (Umlagerung). All that we can state with any degree of certainty is that oxybenzylalcohol, by a process of dehydration, loses water and turns into ill-defined resinous bodies designated under the generic name of saliretins. To try to establish nearer the structural constitution of their molecules is out of the question. That the gradual elimination of water should decrease the fusibility of these bodies and accentuate their insolubility, seems almost self-evident to any chemist and requires no further explanation.

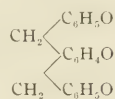
DeLaire was the first, by his published patents (DeLaire, D. R. P., 189,262; British Patent, 15,517, 1905; French Patent, 350,180) to demonstrate the obvious relation of the so-called fusible condensation products with phenol alcohols and saliretin resins, by showing that these phenol alcohols can be transformed industrially by dehydration into fusible resins or saliretin products suitable for commercial purposes, in place of shellac, copal or other natural resins. He showed, furthermore, that in this process, it is not necessary to first produce the phenol alcohol in pure form, but that the two succeeding reactions (condensation and further dehydration with formation of saliretin resins) can be carried out practically at the same time, so that the phenol alcohol is dehydrated to saliretin as soon as it forms.

As stated above, direct experiments in my laboratory have conclusively shown that even when hydrochloric acid is used as condensing agent, in presence of phenol and formaldehyde, notable amounts of phenol alcohol are formed at first, which soon undergo complete resinification by further application of heat.

These fusible resins, or saliretin products, are practically identical with those described by Blumer a few years earlier (Louis Blumer, British Pat., 12,880, 1902). However, the relationship of these fusible resins might escape notice by the fact that these resins are generally more fusible and soluble than pure saliretin; furthermore, these artificial resins do not, on further application of moderate heat, lose their fusibility, unless under special conditions. But these differences are merely due to the fact that the commercial resins of the Blumer or DeLaire fusible type always contain more or less free phenol or cresol, which forms a solid solution and confers upon them higher and more permanent fusibility. I have already published the fact that if this excess of phenol is removed by suitable means, the fusibility and solubility of these substances is soon impaired (Eighth International Congress of Chemistry, New York, September, 1912; *THIS JOURNAL*, **4**, No. 10) and the fusible resin behaves then generally as the pure saliretin resulting from the dehydration of pure phenol alcohol.

The above-mentioned facts, easy to follow, give us a rather simple practical interpretation as to the chemical parentage of the so-called fusible, soluble phenol-formaldehyde resins, so that we can consider them as saliretin products, or so-called dehydration products of the corresponding phenol alcohols. However, this is about as far as we can go. As soon as we try to propose any theory about their molecular structure, we leave the terra firma of established facts, and we enter the nebulous realm of gratuitous assumptions and hypothesis.

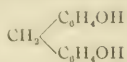
Mr. J. W. Aylsworth (U. S. P., Aylsworth, 1,020,593) forms the fusible soluble resin by direct action of three molecules of phenol on two molecules of formaldehyde, without condensing agents. He calls this substance "phenol resin," and assumes its constitution to be



In discussing the latter formula, Dr. H. Lebach (*Soc. Chem. Ind.*, 1913) calls attention to the fact that, outside of the relative proportions in which the ingredients are used, we have no other justification for this formula. Dr. Lebach, furthermore, brings out the fact that in the material obtained after Aylsworth's description, decided amounts of free phenol are known to exist. Mr. Aylsworth's interpretation of the constitution of these fusible resins, may be nearer or farther from the truth than the structure formula proposed by others for these saliretin bodies. Or what is more probable, all these fusible resinous substances may be composed of two or several individual chemical bodies all mixed in varying proportions and forming a colloidal solid solution with each other. This applies to any of these resins, whether they are obtained by direct action of phenol on formaldehyde, or whether they are made step by step by the intermediary formation of phenol alcohol and subsequent dehydration thereof. Some of these substances may or may not be simple dehydration products of phenol alcohols derived therefrom by simple union of several molecules with elimination of water, after the same reaction by which ether or ethyl oxide is formed by the elimination of water between two molecules of alcohol. Or again, the process of dehydration may possibly be complicated by more far-reaching transformations, transpositions, or rearrangements of the molecule.

That diphenylmethan compounds seem to play some rôle in

this reaction is proved by the fact that we have succeeded in isolating from the initial mass of phenol, formaldehyde and hydrochloric acid, appreciable amounts of paradioxydiphenylmethan,



alongside of the oxybenzylalcohols mentioned above. Whether paradioxydiphenylmethan is formed here directly or whether it is the result of the action of initially formed phenol alcohol on a further molecule of phenol, are questions of minor importance in a matter-of-fact interpretation of these complicated reactions.

At any rate, the formation of bodies of the diphenylmethan group seems to be one of the probable accompaniments of that peculiar resinification process, whereby phenol alcohols are transformed by dehydration, into saliretins, or whereby phenol and formaldehyde are directly condensed to the same kind of fusible resins.

Dr. F. Raschig has properly called our attention to the fact [Raschig, *Z. angew. Chem.*, **25**, 1945 (1912)] that in case diphenylmethan derivatives are formed, a large number of isomers can exist and a variety of reactions can take place at the same time, or may succeed each other. He, too, brings out the opinion that it becomes utterly impossible, even with all the means which science has put hitherto at our disposal, to separate and identify these different bodies. We might attempt to do so with products which can be isolated by fractional crystallization, precipitation, or fractional distillation. But with amorphous colloidal bodies, intermixed with each other in solid solution, this becomes a hopelessly impossible task.

Dr. Raschig expressed the opinion that the soluble resin in reality is a mixture of the three isomeric dioxydiphenylmethans, rendered impure by an excess of free phenol, and some of the phenol alcohol corresponding to dioxydiphenylmethans. Unfortunately, this simple interpretation is not substantiated by the fact that the soluble resin, treated with boiling water, does not give off serious amounts of dioxydiphenylmethan, although the latter is very soluble in boiling water, and should, therefore, be readily separated by this method. Even by very careful treatment, merely small amounts of these crystalline bodies can be separated.

Nevertheless, all these fusible, soluble phenolformaldehyde resins described by Blumer, DeLaire, Lebach (Knoll-Wetter), Bayer & Co., Aylsworth, and others, have practically the same chemical and physical properties, differing only in minor details by the way in which they are prepared and by the more or less large amount of free phenol they may contain [Baekeland, *This Journal*, **1**, No. 3, March, 1909; **1**, No. 8, Aug., 1909; **4**, No. 10, Oct., 1912; DeLaire (*loc. cit.*), as well as myself, has also shown how these very same fusible resins are obtainable in pure state by direct dehydration of phenol alcohols, which identifies them practically as saliretin bodies. At the same time, I have been able to point out the great importance of the presence of small quantities of free phenols which tend to insure their fusibility and solubility. Furthermore, I have been able to produce these same fusible and soluble resins by simply heating phenol alcohol or saliretin in presence of some free phenol [Baekeland, *This Journal*, **1**, No. 8 (1909)].

On the other hand, we have succeeded also in producing a fusible phenol resin by heating for 3 hours at 180° C., 100 grams of paradioxydiphenylmethan with 10 grams of paraform in a sealed tube.¹

By increasing the proportion of paraform, we have succeeded by the same method, in producing a very hard and infusible amorphous colloidal body, of very high resistivity to most chemicals and solvents.

This fact seems to indicate that diphenylmethanphenols

¹ This proportion would correspond approximately to 15 molecules of phenol reacting on 14 molecules of formaldehyde.

may, indeed, be used as a starting point, or may be formed among the transition products, in the formation of the so-called fusible, soluble condensation products, as well as the infusible, insoluble condensation products.

There is, nevertheless, another fact which proclaims eloquently the saliretin-like nature of these fusible phenolic resinous condensation products. The latter can be obtained by reduction of salicylic acid [Baekeland, *This Journal*, **4**, No. 10, Oct., 1912; Velden, *J. prakt. Chem.*, [2] **15**, 164; *Jahresbericht*, 1877, 337].

For the sake of clearness, before leaving the subject of these relatively simple fusible soluble phenolic condensation products, I should mention that I have proposed, heretofore, to designate them all under the generic name of Novolak: this merely as a means for grouping under the same denomination, products of the same composition and properties, although they have been prepared by different methods and described by several other investigators, like Blumer, DeLaire, Lebach and Aylsworth, etc. I believe we can just as well call them fusible saliretin products.

From different sources many attempts have been made as far back as 1902, to utilize these soluble artificial resins, as shellac substitutes, or as substitutes for other natural resins in the manufacture of varnish. In this respect, they were of special interest, a few years ago, when the market price of shellac was unusually high. As far as my own experience goes, and as far as I have been able to ascertain from others, none of these products have fulfilled the expectations of industrial use.

Nowadays, the main importance of these shellac substitutes (Novolak or saliretin resins) resides in the fact that they bear an immediate relationship to another class of bodies, the so-called infusible insoluble phenolic condensation products, which have been designated by such names as bakelite, resinit, condensite, and which Dr. Lebach called "resites."

We shall now try to discuss the chemical constitution of these infusible condensation products of maximum hardness and resistivity.

The very fact that the latter-mentioned bodies are infusible and insoluble, and that they are characterized, furthermore, by a much more pronounced chemical and physical inertness than the so-called Novolak resins or saliretin products, emphasizes still more the unusual difficulty which confronts us in the study of the chemical constitution of these bodies. If it is practically impossible to indicate with any degree of certainty the molecular constitution of the relatively simple saliretin bodies, our task becomes incomparably more difficult here.

Moreover, we should take into consideration that in the industry, these products are made from commercial carbolic acid, containing besides phenol, variable amounts of ortho-, meta-, and para-cresol, and other homologs and isomers. We should also bear in mind that each of these homologs may act differently and not only may produce isomeric bodies, but these isomeric bodies may react one upon another in decidedly different ways, and thus greatly influence the progress of the reaction as well as the physical and chemical properties of the final products.

Under the circumstances, it becomes simply impossible to try to characterize by a general scientific interpretation either the reaction which engenders those bodies, or the molecular constitution thereof. All that we can say, with some degree of probability and without embarking wildly on fantastic hypotheses, can easily be summed up as follows:

First: That these bodies are phenolic condensation products of formaldehyde, or of equivalent methylene-group-containing substances, this condensation process having for result, a corresponding enlargement of the so-called carbon nucleus of the molecule.

Furthermore, it is a well accepted fact that in these reactions,

by them, becomes so limitlessly large that we know of no scientific methods which would enable us to identify them all. Commenting on this fact, he states that the amorphous character, as well as the valuable technical qualities of the end products, are probably due to the great variety of the different bodies which are all contained therein, including at the same time, extraneous bodies like free phenol, etc.

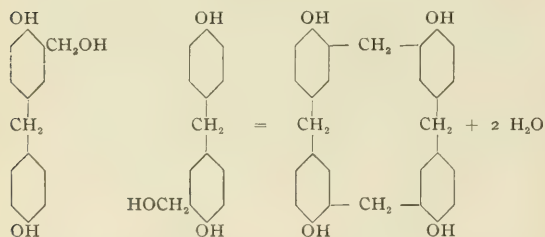
Dr. Raschig seems to infer, however, that the production of the soluble variety resinous condensation products is merely determined by the relative amounts of phenol and formaldehyde. He says: "Der Unterschied zwischen den löslichen Harzversatzmitteln und dem unlöslichen Bakelit besteht nun im wesentlichen darin, dass man bei Herstellung der ersteren auf 1 Mol. Phenol weniger als 1 Mol. Formaldehyd, in der Regel nur 0.5 Mol., beim letzteren aber mindestens 1 Mol. Formaldehyd, in der Regel 10-20% mehr zur Anwendung bringt." And he goes on to state that in case insufficient formaldehyde be used, a mixture of the three isomeric dioxidiphenylmethans should be the result, while if more formaldehyde is present, then the corresponding phenol alcohols of those dioxidiphenylmethans will be formed; the latter can react further upon another, and in this way build up a much larger molecule which accounts for the insolubility and great resistivity of these large molecules, of which the dynamics are correspondingly decreased.

I take the liberty of pointing out that this theoretical interpretation holds good only to a certain extent. If it is possible, and even probable, that some of the bodies mentioned by Dr. Raschig exist in the first phases of the reaction, or may exist in the final products together with an endless variety of other chemical individuals, we know next to nothing of the relative importance thereof, whether they exist as traces, or whether they play a fundamental rôle.

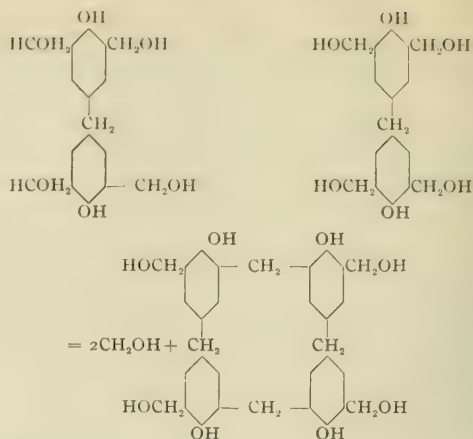
Furthermore, in his generalizations, in relation to the influence of relative quantities of phenol and formaldehyde, Dr. Raschig seems to overlook the very important and well established fact that the nature of the condensing agent has an enormous influence on whether fusible or infusible products will be formed. For instance, it is known that if you operate in presence of small amounts of bases, infusible condensation products will be the result, whether you use an excess of phenol or not [Bakeland, *THIS JOURNAL*, 1, No. 8, (1909); 4, No. 10 (1912)].

In addition to the foregoing, we should not lose sight of the possibility that in all these rapidly succeeding reactions, we may have several cases of rearrangement or transposition of the molecule (Umlagerung).

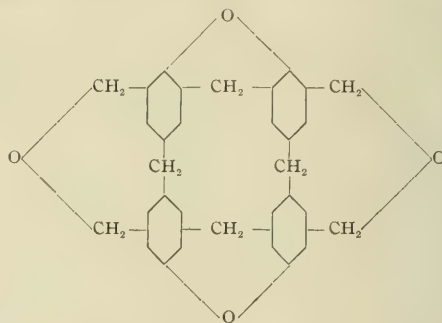
Dr. Raschig has outlined some further theoretical interpretations from the standpoint of the assumption that diphenylmethan derivatives are the main products in this process. He has shown, for instance, how under certain conditions a body may be conceived which he calls Bakelite I



and then again another body resulting from a larger proportion of formaldehyde,



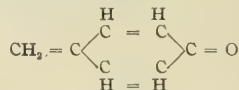
which after dehydration gives a molecule which Raschig calls Bakelite II:



Much as these speculative considerations, presented by a scientist of reputation, may be able to give us food for thought, we must not forget that one hypothesis is about as easy to propose as another as long as we are unable to use any of the methods for determining molecular size and molecular constitution.

Even Dr. Raschig warns us, with the natural conservatism of an able chemist of long and wide experience, when he says: "Ueber die Chemie des Bakelits tapen wir noch vollständig im Dunkeln."

Of late, Wohl (*Berichte*, 45, 2046) has advanced a radically new hypothesis which considers these bodies as polymerization products of methylene derivatives of the tautomeric phenol,



and he advanced this opinion after the study of acrolein derivatives of phenols and of the so-called resorcin ethers.

Before leaving this subject, I should mention that we have tried to verify the statement of Dr. Raschig that orthoxybenzylalcohol, treated alone with a condensing agent, does not furnish bakelite, and that paraoxybenzylalcohol acts in the same way while bakelite is produced with its characteristic insolubility from the mixture of both. He deduced from this that both para- and orthocompounds are needed for the production of bakelite. In a footnote, however, he mentions that both ortho- and paraoxybenzylalcohol, after long heating, furnish bakelite of typical insolubility in alkali; but that the reason for this is to be found in the fact that both phenol alcohols split by and by

in formaldehyde and phenol which then can unite again and form the other phenol alcohol, so that finally a mixture is formed of ortho- and paraoxybenzylalcohol.

The paraoxybenzylalcohol used in our own experiments was mostly prepared by Auwers' method and had a melting point of 110° C. to 112° C. Auwers and Daecke (*Ber.*, **32**, 3374) indicate 124.5° C.-125.5° C. as the melting point of paraoxybenzylalcohol, while Manasse (*Ber.*, **27**, 2411) and Lederer (*J. prakt. Chem.*, [2] **50**, 225) indicate 110° C.

We found that when orthoxybenzylalcohol (saligenin) or paraoxybenzylalcohol, or a mixture of equal parts of both together with a small amount either of ammonia or of caustic soda is heated in a sealed tube to 160° C. for about 6 hours, products are obtained which are practically the same and which are identical in their properties with the so-called polymerized saliretins. Indeed, they are all considerably inferior in chemical resistivity to bakelite of highest hardness and resistivity. They soften on heating, but are infusible, are much more brittle than the hardest obtainable products of the kind, and begin to break up immediately, without dissolving, when treated with acetone or with 20 per cent caustic soda.

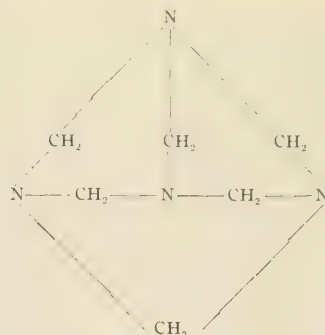
On the other hand, when paraoxybenzylalcohol is mixed with 5 per cent paraform (this corresponds about to the proportions of 6 mols. phenol to 7 $\frac{1}{4}$ mols. formaldehyde) and heated in a sealed tube, decidedly different products are obtained which not only are infusible, but do not soften by application of heat, and are as hard as the hardest and most resistive bakelite, and are not attacked by acetone or by 20 per cent caustic soda.

It seems, therefore, that the products obtained by Dr. Raschig belong to that variety which I described as polymerized saliretins, and which do not possess, by any means, the maximum hardness nor chemical resistivity of the products which are formed whenever there is sufficient formaldehyde or equivalents thereof present [Baekeland, *THIS JOURNAL*, **4**, No. 10 (1912)].

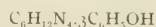
In whatever theoretical speculations we engage on this subject, we must not lose sight of the fact that the nature of the condensing agent may have an enormous influence on the way the reaction takes place, even if at the end the products may look very much alike and be more or less identical.

For instance, when an acid condensing agent is used, the process seems to proceed very differently from what happens when alkalis are used (Baekeland, *loc. cit.*). Then again, when ammonia is used, the reactions which succeed each other seem to be quite different. In the latter case, they can be followed to quite an extent [Lebach, *Z. angew. Chem.*, **22**, 1601 (1909)].

For instance, every chemist knows that ammonia on acting on formaldehyde produces immediately hexamethylentetramine:



In the same way, if ammonia be added to a mixture of phenol and formaldehyde, the same hexamethylentetramine is formed independently whether the phenol or the ammonia be added first or last. In presence of the phenol, one molecule of hexamethylentetramine adds to three molecules of phenol and gives



hexamethylentetraminetriphenol (Tollens and Moschats, *Liebigs Ann.*, **272**, 280; Wohl, *Ber.*, **19**, 1892; Tollens, *Berichte*, **17**, 643; Carl Goldsmith, *Verlage von Friedrich Cohn*, **1903**, 29; Cambier, *Brochet Compt. rend.*, **120**, 557; Lebach, *Z. für angew. Chem.*, **1909**, 1600; Beilstein, *Handb. der Organ. Chem.*, **2**, 37, 651).

Under the action of heat, this latter substance decomposes and sets free large amounts of ammonia gas, leaving finally a hard, infusible body. But the ammonia can act immediately on new amounts of formaldehyde, and repeat the same reaction so that a small amount of ammonia is sufficient to act as catalytic agent for all the formaldehyde present, and to carry on the whole reaction to the finish, after which free ammonia is found in the product.

The general reaction seems to be the same whether ammonia and formaldehyde be used in conjunction with phenol, or whether phenol be made to react directly on hexamethylentetramine or whether hexamethylentetraminetriphenol be decomposed by heat. In the latter case, however, the final product is very porous and does not present a colloidal mass sufficiently homogeneous for technical purposes. On this account the use of a somewhat larger amount of phenol or other suitable similar body becomes imperative, so as to obviate this defect. Hence, some excess of phenol, or suitable solid solvent, will accomplish technical results which are not otherwise possible when hexamethylentetramine is used alone.

VONKERS, N. Y.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE ELECTROCHEMICAL INDUSTRIES OF ITALY

The last report of the "Società Italiana d'Elettrochimica" contains an account of the status of the electrochemical works and of the developments during 1912.

The second Pescara waterfall was brought into work during 1912, and electric power, at a voltage of 80,000 to 88,000, was conveyed to Naples at the close of the year. The production of sodium hydroxide at the Bussi Works amounted to 3,500 metric tons. The production at the commencement in 1905-1906 was only 1,820 tons; but it now seems that the limit of the capacity of the plant has been reached. Attention is being directed to the manufacture of chlorinated products, for which the works is utilizing all the chlorine, but a regular market has not so far been found. There was a considerable increase in the

production of hydrochloric acid, for which there are many markets in Italy, and carbon tetrachloride was exported. Notwithstanding these developments, the profits of the works were somewhat less than those of the previous year, namely, 336,498 instead of 350,877 lire; this is attributed to the high cost of fuel, and electric boilers are now about to be installed with a view to economy.

THE MATCH INDUSTRY OF SWEDEN

It has been announced that ten of the twelve independent match factories in Sweden, which have remained outside the so-called Swedish match trust, are to be formed into a single corporation to be known as "Aktiebolaget Förenade Svenska Tändsticksfabriker." The annual output is to be 8,000,000

boxes as compared to the 2,400,000 boxes now produced by the Jönköping-Vulcan factories.

The Jonköpings och Vuleans Tändsticksfabrik was formed by the large concerns at Jonköping and Tidholm to prevent undue competition and to aid the export trade. Nine-tenths of the matches produced are exported, largely through London and Hamburg, although the interests have encountered high protective duties in most countries.

The phosphorus, antimony, sulfur and paraffin used are imported, but potassium chlorate is obtained from the Swedish manufacturers. Much of the aspen wood used is imported from Finland and Russia. The success of the industry is due largely to the employment of devices for replacing manual labor; "complete machines" producing 3,600 boxes of matches per hour have been in use since 1892.

THE RECOVERY OF BRASS FROM FOUNDRY CINDERS

Wittich (*Eng. Min. J.*, 95, 853) describes the process of reclaiming brass contained in the cinders from brass foundries. The recovery of such brass particles, heretofore almost completely lost, has been found to be satisfactory in eleven plants in this country, and the largest installation for the purpose is now being made by the Michigan Smelting & Refining Co., of Detroit, Mich. The accompanying flowsheet shows the plant in course of construction at Detroit.

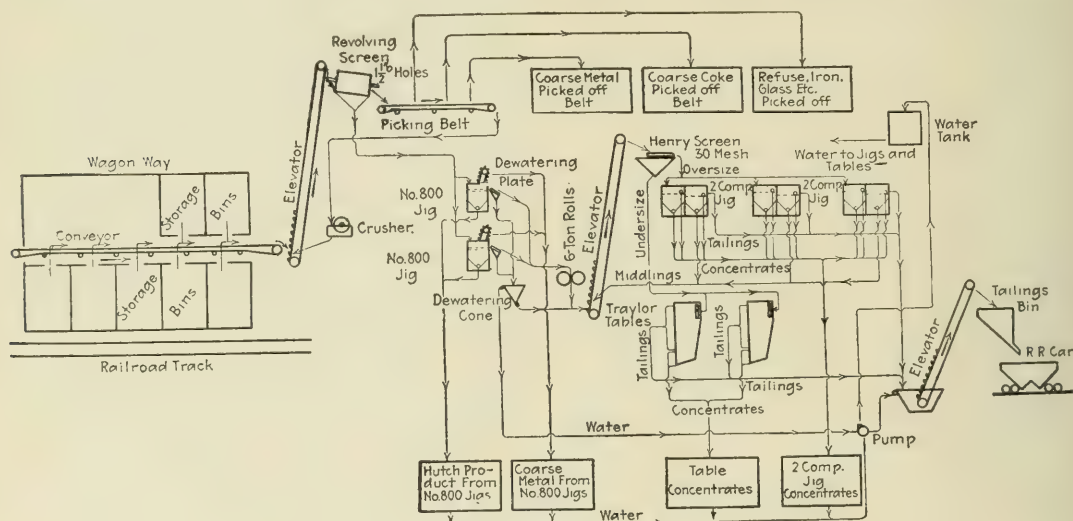
The plant will have a capacity of 75 tons daily. The original feed will carry from 3 to 5 per cent of metal, while the con-

Undersize from the $1\frac{1}{2}$ in. trommel goes to a pair of bull jigs, each of single compartment, 36×48 in., operated by double eccentrics, at 75 r. p. m. The hutch product from the two bull jigs carries from 25 to 30 per cent brass and goes to a bin, ready for the crucible. A rotating valve at end of jigs gets the coarse metal. All tailings from the bull jigs are reground. They first pass over dewatering plates, the dry tailing passing to a set of rolls, and the water going to a dewatering cone. Both the reground tailings and the sediment from the cone pass to an elevator, thence to a 30-mesh Henry shaker screen. The oversize goes to three sets of two-compartment gast-motion jigs, each compartment being 24×36 ft. Double eccentrics have 175 r. p. m. The undersize passes to hopper, hence to two Traylor tables.

Tailings from the three fast-motion jigs and from the tables pass through launders to a hopper, are elevated, and stored in a bin, ready for removal in railway cars to be used as ballast or for other purposes. Middlings from the fast-motion jigs return to the elevator and are retreated, after passing through a set of baby rolls which are not shown on the flowsheet, this change having been decided on after the first plans were drawn.

AN ELECTROLYTIC THEORY OF THE CORROSION OF IRON

In a paper read before the Faraday Society at the Manchester meeting on April 4, 1913, Bertram Lambert (*Chem. News*, 107, 184) expressed his inclination to the view that substances which protect iron from corrosion have the power of destroying or



PLANT FOR RECOVERING BRASS FROM CINDERS

concentrates will carry from 25 to 50 per cent metal. The loss of metal in the tailings, it is estimated from operations at other plants, will be less than $\frac{1}{2}$ per cent. The metal recovery should be close to 7000 lbs. daily when the plant is operated at full capacity.

Beneath the receiving bins a conveyor belt, automatically fed, carries the cinders to an elevator, and thence to a revolving trommel. The oversize from the screen, which is 1 1/2 in. mesh, goes to a hand-picking belt, which is 36 in. wide and which revolves slowly. The coarse, heavy cinders passing over the end of the belt go to a 15 in. Blake crusher, and thence return to the 1 1/2 in. trommel.

The heavy, coarse metal picked off the belt goes to a bin, and is ready for the crucible. The coarse coke goes to a bin and can be used in smelting. The refuse goes to the dump.

reducing the electrical differences which always exist in commercial forms of iron—that they have a passivating effect—and that the substances, such as the chlorides of the alkali metals which stimulate corrosion do so by augmenting these electrical differences. It is well known that ordinary commercial iron is rendered passive by certain substances, *e. g.*, nitric acid, solutions of the caustic alkalis, or chromic acid, and that such passive iron, so long as the passivity persists, will not rust in contact with pure water and pure oxygen, and will not cause the deposition of copper from very dilute solutions of cupric sulfate. Lambert considers that it seems probable that these substances have the power of altering the surface of commercial iron so as to destroy, temporarily, the electrical differences on its surface—to produce what might be described as an “electrically equable” surface. The result of this would be that the iron would possess

no tendency to go into solution in an electrolyte, and consequently would not rust when placed in contact with air and water. Since passivity can be produced by widely different substances, he thinks it not improbable that the "electrically equable" surface produced is not always of the same nature.

THE USE OF CAST IRON BRIQUETTS IN GERMAN FOUNDRIES

Hugo Matz (*Chem. Ztg.*, 37, No. 37, 375) considers that the introduction of the use of cast iron briquettes is an innovation which has had a revolutionary effect in the iron industry, since these briquettes have made it possible to produce castings of high grade without employing specially expensive pig iron. At first, there was considerable opposition in the trade to their use, but Matz states that this has now been overcome in the German foundries.

Those foundries making a specialty of locomotive parts were the first to adopt the use of briquettes; extensive experiments have shown that steam cylinders manufactured by the addition of 15-30 per cent of briquet-chips to the castings, are of the same grade as those made from the special pig irons imported from England and Sweden. One great advantage derived from the use of the briquettes is a material reduction of carbon.

According to analyses made in the laboratories of the Sächsischen Metall-Brikettwerke, the composition of the briquettes is as follows: Silicon, 1.8 to 2.0 per cent; manganese, 0.6 to 0.8 per cent; sulfur, 0.10 to 0.13 per cent; and phosphorus, 0.7 to 0.9 per cent.

THE BISULFITE PROCESS FOR THE EXTRACTION OF ZINC

The bisulfite process, as practised at the works of the British Metals Extraction Co., Ltd., at Llansamlet, Wales, is described in *The Engineering and Mining Journal*, 95, 792. The ore, after pulverization, is roasted in mechanical furnaces, the sulfur dioxide being conveyed from the roasting furnaces to the extraction towers. The roasting is done very slowly, 24 hours being required to finish a charge.

The roasted ore is conveyed to the top of a specially designed tower where a weighed amount is mixed with a weighed amount of water, so as to form a thin pulp. This pulp descends through the tower, meeting the sulfur dioxide coming up. The agitation produced by the interior construction of the tower brings about such an intimate and effective contact of the pulp with the sulfur dioxide that by the time the pulp reaches the receiving tanks at the bottom of the tower nearly 90 per cent of the zinc has been extracted. The solution of zinc bisulfite is drawn off into an apparatus, wherein it is heated, precipitating zinc monosulfite. The latter is calcined, yielding zinc oxide, which goes to spelter furnaces, the Villiers works having been purchased for smelting it. In that works spelter assaying 99.85 per cent zinc is produced; this spelter is said to bring about \$20.00 per ton more than ordinary spelter. The extraction of zinc in the bisulfite process proper is said to be from 84 to 89 per cent in the case of the better roasted charges. In the treatment of ore containing 28 per cent zinc, the residue, which goes to the lead smelter, contains about 8.5 per cent zinc.

THE TOXICITY OF LEAD PAINTS

In 1911, Baly (see *Oil and Colour Trades J.*, May 6, 1911, 1518; *Chem. Trade J.*, May 13, 1911) stated that "a definite volatile lead compound is given off in the drying of white lead paint. It appeared to be peculiar to basic carbonate of lead and to explain the prevalence of lead poisoning among painters." Later, Baly (*J. Soc. Chem. Ind.*, 31, 515) again referred to the toxicity of white lead; he claimed that his experiments established the fact "that a poisonous volatile substance is given off paints made with white lead or red lead."

Armstrong and Klein (*Idem*, 32, 320), after a full consideration of the subject, conclude:

1. That the vapors produced during the drying of white lead pastes and paints do not contain lead.

2. That the vapors given off as paints dry consist of turpentine, for the most part, together with oxidation products of the oil, and that these latter are common to paints generally containing oil so treated that it will dry.

3. That the oxidation products formed from the oil during drying are harmless under the conditions of practice, as shown by experiments upon animals.

4. That the toxic effects sometimes experienced from drying paints are to be ascribed to turpentine and that due allowance must be made for this in dealing with the hygienic phase of the problem. Their inquiry also shows that in many cases effects have been regarded as due to "lead poisoning" which are attributable to other causes, especially to turpentine.

5. The whole available evidence indicates that the dangers attending the use of lead compounds are only the well-known mechanical dangers.

6. There is no foundation for the importation of a new element of danger into the consideration of the question of paints. Lead paints are to be objected to only on the ground that they may enter into the system through careless handling or in the form of dust such as is produced by rubbing down old paint.

THE POTASH SITUATION IN AUSTRIA

While it is hardly to be expected that the Austrian potash deposits, said to be the only ones of apparent importance outside of Germany, will be able to compete with those of the latter country, either now or in the future, *The Chemical Trade Journal*, 52, 393, reports that there is every prospect that they will be exploited on an efficient scale in the near future. A combination has been organized for the purpose of working the potash measures in the Calicz district and abutting areas, and it is hoped to be able to supply this fertilizer to a large portion of Austria at reasonable prices and at the same time to pay a remunerative dividend. The concession on which the new combination will work is to extend over a period of fifty years, and the interests of the Austrian consumer have been protected by a special clause requiring that certain limits in sale prices shall not be exceeded for domestic transactions. It is hoped, also, on behalf of the inland consumers, that the Austrian Government may be induced to impose a high export tariff on goods sold outside the country, the object being to reduce the price to consumers to a lower level even than the limit beyond which the exploiters may not invoice their goods. It has required a long time to effect this combination; but considerable political difficulties had to be overcome in respect to the Government's monopoly claim, which extends to the salt deposits of the country, in close association with which the potash deposits are found. This can, it is said, be got over by certain conditions attaching to the sale of the salt produced along with the potash. This will be the first commercial test of the value of the Austrian potash reserves.

WASTE SULFITE LIQUOR AS A FERTILIZER

The fact that waste sulfite liquor contains a large amount of organic matter and certain chemical compounds of value as plant foods has led, at various times, to experimental investigations as to its employment in agriculture. According to *Paper*, May 7, 1913, the subject has recently received full consideration in Germany. A contributor to *Fühling's landwirtschaftliche Zeitung*, 1913, No. 4, found that a cellulose mill of medium capacity, producing 500 cubic meters of waste liquor daily, was discharging 50,000 to 60,000 kilograms of organic matter in a dissolved state into a stream, to its manifest detriment, particularly in the summer. After giving the matter

consideration for several years, it was concluded that the employment of this waste organic material in the enrichment of soils deficient in humus was the best purpose for which it could be used. At first, it was feared that the calcium sulfite contained in the liquor would have an injurious action on plant life, as it is well known that free sulfurous acid has a detrimental effect on the formation of chlorophyll in leaves. As a result of investigations in this direction, steps were taken to neutralize the liquor so as to prevent the discharge of the waste water in an acid condition, as a result of which it was found that the liquor no longer exercised injury to the plant life on the fields irrigated therewith. During 1911 and 1912, Thalau made further investigations into the effects of neutral sulfite of lime on vegetation, and found that, when introduced into the land, plants were not injured in the case of loamy or sandy soils. In high marshy soils injurious effects could be detected, probably owing to the decomposition of the calcium sulfite by the humic acid. Some experiments made in open field and in a plant laboratory, in which dried waste liquor was used on potatoes, showed that there was a decided increase in the yield; but it was found that when the waste liquor was used where large amounts of nitrogen were available, a reduction in the yield might result. The conclusion reached was that the waste liquor should not be used as a fertilizer on soil rich in humus and containing a quantity of nitrogen, but that it could be used to advantage on soils poor in humus.

[The spent liquors from the manufacture of sulfite cellulose have frequently been used, after treatment, for manurial purposes, but they are difficult to transport and the soil is capable of assimilating only a limited quantity. Knosel (*Chem. Ztg.*, **26**, 229) devised a process wherein the liquors were concentrated and then mixed with an approximately equal weight of Thomas slag-meal; but Ahrens (*Chem. Centr.*, **1905**, I, 700) considered it of no value. Hoesch et Cie have patented a process (French Patent 434,943, 1911), in which waste sulfite liquors are treated direct, or after concentrating or evaporating to dryness, with nitrogen-fixing bacteria; it is claimed that the material forms an advantageous medium for the culture of the bacteria.—W. A. H.]

THE DISPOSAL OF THE DISCHARGES FROM PACKING-HOUSES

Screening the sewage and factory wastes discharged into the "Bubbly Creek" arm of the Chicago River by the stockyards and packing-houses is to be tried as a means of avoiding the deposit of solid matter in the river and the drainage canal. Chemical and sedimentation treatments have been proposed by the Sanitary District of Chicago in order to improve the character of the discharges from a sanitary standpoint, but at present only the screening will be tried. There will be two rotary screens of the Weand type: one will handle the sewage from four of the larger packing-houses and the other will handle that from the pens of the stockyards. This installation is experimental, and if it proves successful it is probable that all the sewage will be treated in this manner. No plans have been made as yet for the disposal of any large quantity of solid matter removed by the screens.

SUBSTITUTES FOR GASOLINE

"The waning supply of gasoline," a state of affairs occasioned by the rapid and apparently undiminishing increase in the use of petrol-driven motors, has recently been the subject for serious discussion in the technical press. In fact, the question of meeting the increase in the consumption of the more volatile petroleum products is the vital issue of the day in the industry and a matter of deep concern to the engineer. Some of the very recent opinions on the matter follow.

Lewes (*Chem. World*, **2**, 113) considers that in the not very distant future it will be to alcohol that we shall have to turn,

and that it will then be found that alcohol denatured with 10 per cent of benzol will give a motor spirit at once safer, more pleasant to use, and sweeter in exhaust than the petrol in use to day. While the calorific value of such a mixture is only 0.6 of the value of petrol, Lewes is of the opinion that the smaller amount of air required, the increased explosive range of the mixture, and the higher compression that could be used in the cylinder, all combine to make it the ideal motor spirit.

The opinion of Lewes represents the English view point. Less and less petrol is being exported from the United States, owing to the increase in the domestic consumption; and it is a certainty that unless some other source can be found to supply a large proportion of England's needs, prices must rise, and every possible method of creating such a supply is being eagerly passed under review.

Since benzol in running is 12 per cent more powerful than petrol, and as regards elasticity and starting is quite as good, this is being favorably regarded in England as a petrol-substitute. The total quantity of benzol recovered in the English coke-oven recovery plants amounts to about 8,000,000 gallons annually and probably over a third of this is exported. Before it is fitted for motor use, commercial benzol, which usually contains about 140 grains of sulfur per gallon, must be carefully purified.

Secor (*Sci. Am. Suppl.*, **75**, 271) points out five different methods of increasing the normal visible supply of gasoline: (1) Importation; (2) Increasing the total yield of American crude petroleum; (3) The production of gasoline from kerosene; (4) The production of natural gas gasoline; and (5) By lowering the specific gravity of commercial gasoline. With the exception of importation these various methods of augmenting the available supply of gasoline are in active operation, and every increase in the price is a stimulus to additional output. The Standard Oil Company has imported some Russian naphtha, but no more is available. The price of gasoline in Russia has increased 100 per cent in the last two years, which state of affairs has warranted the Russian Government in promoting the production of alcohol. The Shell Oil Company of England has shipped some gasoline from Borneo to Canada, but the total quantity available abroad is insufficient for home needs, and America is still exporting gasoline at the rate of 15 to 20 million gallons per month.

Secor considers that alcohol can be used advantageously if gasoline advances to 20 to 25 cents wholesale. While special engines are required, "there is no reason why alcohol should not be used to-day in cars selling around \$5,000." He looks upon kerosene as the best fuel, since, from his view as an automobile engineer, it combines more advantages than either gasoline or alcohol.

Engine builders have evolved a system whereby kerosene and gasoline are combined as to ensure high volatility, with a minimum deposition of carbon; and it is of interest to note that the new fuel of the Standard Oil Company, the "Motor Spirit," obtained by a process devised by W. M. Burton, has a greater range of boiling points than gasoline, allowing, it is said, the motor to be started more easily. "Motor Spirit" is said to be cheaper than gasoline and to furnish 25 per cent more mileage.

ARTIFICIAL LEATHER FROM "SYROLIT"

In 1909, Schütze, of Riga, Russia, found that a material strongly resistant to acids and suitable for employment for insulating purposes might be manufactured from milk curds. According to his process, the milk curds are made into a paste with cold water, with the addition of coloring matter if desired, and then heated at 100° C. for about ten minutes, being meanwhile continuously stirred until the material assumes a pulpy state. The hot pulp is then subjected to a pressure of at least five kilograms per square centimeter, in previously heated molds, for about three hours, and immediately immersed in formalin

for a period of three to four days. W. J. Luxmoore, of London, now finds that artificial leather may be manufactured from this product, which is marketed under the name "Syrolit," by incorporating with it rubber, gutta percha, etc. The composition is rolled through pattern rollers in order to imitate the surface of leather.

RUBBER IN HAWAII

According to *Rubber World*, 7, No. 158, 8, rubber is steadily becoming an important Hawaiian product. On the island of Maui many trees have been planted and these are being tapped in large numbers. Steady efforts are being made to improve the methods of preparation in order to increase the marketable value: 35,000 trees were tapped during 1912, and altogether some 8,000 pounds of rubber were produced, most of which was exported. For 1913, an output of 20,000 pounds is anticipated. Attention has been directed to an indigenous rubber tree (*Euphorbia lorifolia*) which grows in several localities; one place in particular on the Island of Hawaii has 6,000 trees averaging 75 trees to the acre, whose product is 14-17 per cent of rubber and 60 per cent of resin (chicle). It is reported that the latex contains 42 per cent of solid material and that one man can collect 16-30 pounds of crude product per day.

Die Chemische Industrie, 36, No. 7, 205, also refers to the cultivation of rubber in Hawaii. According to this journal, the available statistics are as follows:

Company	Founded	Capital	Planted territory in acres
Nahiku Rubber Co.....	1905	\$150,000	480
Hawaii-American Co.....	1905	\$ 50,000	245
Koolan Rubber Co.....	1906	\$ 30,000	275
Nahiku Sugar Co.....	1906	250
Pacific Development Co.....	1907	\$ 80,000	250

THE USE OF "HUMIN" IN THE PURIFICATION OF SUGAR FACTORY WASTE WATERS

In the beet sugar factory the waste waters from the washers, the diffusion battery, and the chip presses are usually purified by simply liming and settling. This has been said to be unsatisfactory, owing to the occurrence of putrefaction, hydrogen sulfide being evolved and the water darkened. In 1911, Thein (*Deut. Zuckerind.*, 36, 286) stated that excellent results had been obtained by the use of the Hoyermann-Wellensiek process, which consists in the use of a preparation termed "Humin," obtained by treating brown coal rich in humic matter with sodium hydroxide. He reported that when the "Humin" was mixed with warm condenser water, using a sufficient volume of this to impart a light brown color to the waste water, and then liming to weak alkalinity, a voluminous precipitate was obtained, which rapidly subsided, leaving the water clear and practically free from bacteria.

Andriik and Stanek [*Z. Zuckerind. Böhm.*, 37, 282 (1913)] conducted an elaborate investigation of the process of Hoyermann and Wellensiek, and have been led to conclude that the employment of "Humin" and lime does not effect any greater purification of sugar factory waste waters than is accomplished by the use of lime alone.

"CELLOPHANE"

Müller (*Chem. Ztg.*, 37, No. 40, 404) regards "Cellophane" as a "Viscose" product of the highest technical importance. It is prepared by precipitating a xanthogenate solution with ammonium chloride. Colorless films about 0.02 mm. in thickness may be obtained from "Viscose" solutions, and these are marketed in rolls, uniform in thickness and width; the weight of a square meter varies from 15 g. upwards to 1600 g., according to requirements. In preparing the heavier thicknesses, two or more layers are worked up together. The elasticity of "Cellophane" is said to be remarkable; the films are also impermeable

to water, oils and gases, and are non-inflammable and non-explosive. Paper coated with "Cellophane" is claimed to possess more technical advantages than lead, tin, zinc and aluminum ("Alolit") foils, mainly owing to its lightness, non-oxidizability and cleanness; in addition, Müller states that it is gas-tight. "Cellophane" is insoluble in water and alcohol, and it may be treated with boiling water without indications of decomposition. It is not altered when heated to about 120° C. Like "Guadafil" (see Baroni, *Giorn. Farm. Chim.*, 60, 239), "Cellophane" is particularly important because of the fact that the films can be made into any desired shape by softening in, say, water and drying after molding to the proper form.

SAFETY FUSES AND DETONATORS

The *Chemical Trade Journal*, 52, 417, reports that important extensions are being made to the Regent Factory at Linlithgow, belonging to Nobel's Explosive Company. This factory is devoted entirely to the manufacture of safety fuses for use in connection with the various high explosives which are manufactured at Ardeer in considerable quantities—dynamite, blasting gelatine, gelignite, samsonite, carbonite, monobel powder, lyddite, cordite, ballistite, guncotton, etc. At Westquarter, Polmont Station, the company has a factory for the manufacture of detonators.

The safety fuse consists of jute yarn spun around a central core of black gunpowder, and waterproofed by a coating of pitch and gutta-percha. A thin red strand runs through the powdered core. The fuse varies in diameter from $\frac{1}{8}$ to $\frac{1}{4}$ of an inch. The core is of fine-grained gunpowder, which, on ignition, burns evenly at a slow rate, conveying fire to the charge or detonator in the case of high explosives. It is said that much care has to be exercised in the formation of this core to prevent gaps and also to ensure evenness of the time of burning. Generally, ten jute yarns are spun so as to enclose the powder as it flows down from the nozzle of the hopper, and a number of threads are in turn spun around these in the opposite direction. Coatings of specially prepared pitch compounds or gutta-percha are subsequently applied to the semi-manufactured fuse or "rod" thus formed, with a further layer of threads or tape. The surface coating is a varnish of pitch, china clay, or some colored compound. Samples of the finished fuse are tested to make certain that the rate of burning is correct. In this connection, X-rays have been found to be exceedingly satisfactory, immediately detecting irregularities in the powder core.

As regards the speed of burning, the rate is generally about 90 seconds per yard; but for South Africa it is slower—about 100 seconds per yard. Safety fuses are divided into two classes—those for use in dry ground, and those which must be waterproofed, either for submarine work, for placing in wet bore-holes, or for open work in rainy seasons.

At the Westquarter Factory detonators are turned out in extraordinary quantities annually. Fulminate of mercury in a copper tube is the basis of the detonator, which is fired by means of high- or low-tension fuse, or a safety fuse. Made in six sizes, the charge of fulminate for the detonators ranges from 8.3 grains in detonator No. 3 to 30.9 grains in No. 8.

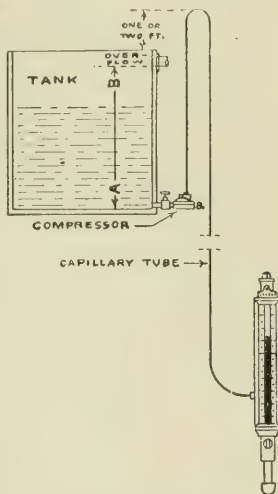
ESTIMATING ON THE COST OF POWER PLANTS

F. W. Gay (*J. Worcester Polytechnic Inst.*, March, 1913) gives an important method of checking estimates on the cost of construction of power plants, in which the greatest chances of error are confined to the minor parts of the installation. Gay has compiled data and prepared diagrams covering power plants from 2,000 to 40,000 kw. in capacity. His experience shows that engines and foundations constitute from 33.6 per cent to 61 per cent of the total equipment cost—an average of 50 per cent; boilers, settings and foundations, from 17.25 per cent to 31.5 per cent—average about 25 per cent; piping, complete, from 7 per cent to 17 per cent—averages about 11 per cent; condensers,

complete, with foundations and auxiliaries, 10 per cent to 15 per cent—average about 11 per cent, circulating water system, 4.5 to 8 per cent—averages about 6.5 per cent. This is a minimum of 72.35 per cent of all apparatus items, leaving the remainder, 27.65 per cent, to be divided among at least eleven groups, including "miscellaneous." Therefore, the greater part of the allowable time should be spent on these five groups. Gay finds it possible to estimate as close as 3 per cent on boilers, installed; on engines, installed, as close as 5 per cent; on engine foundations, as close as 10 per cent; on circulating-water systems, as close as 15 per cent; on piping systems, as close as 20 per cent; and on condensers, auxiliaries and foundations, as close as 3 per cent. Buildings for this apparatus vary from 6 per cent to 16 per cent, an average, say, of 10 per cent.

THE "HYDRO-CATOR"

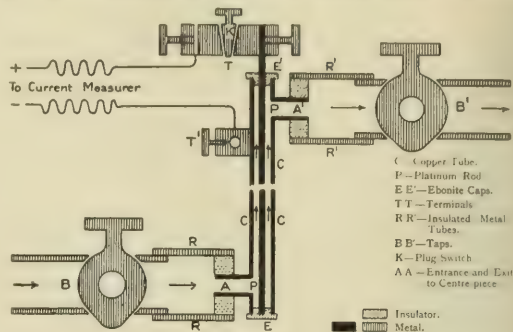
A new type of gauge for indicating liquid levels, termed the "Hydro-Cator," is being manufactured by a Detroit, Mich., company. It is claimed that by using this gauge the height of all kinds of liquids in tanks and reservoirs may be accurately indicated. The instrument is described as a fluid gauge having no mechanical parts; it is actuated by the pressure or weight of the liquid contained in the tank upon an attached compressor, which is connected by capillary tubing, containing air only, with a gauge calibrated in feet and inches. The "Hydro-Cator" may be placed either above or below the tank or reservoir. When located below the tank, as is shown in the figure, the capillary tube is run directly above the tank one foot or more before leading down to the instrument. The compressor may be connected to the outside of the tank or lowered down on the inside; in either case its base must be level with the inside bottom of the vessel.



THE RIDEAL-EVANS CHLOROMETER

The Rideal-Evans electric apparatus for the automatic indication of chlorine, ozone and other oxidizing sterilizing agents in solution is diagrammatically illustrated herewith. It consists of a copper tube, C, 3.5 cm. in length and 4 mm. internal diameter. Within this, running axially through it, is a platinum rod, P (diam. 1 mm.), which is insulated at the two ends from the copper tube by two ebonite caps, E, E'. Liquid is allowed to enter the instrument by the side tube BA and to leave it through A'B'; taps are provided at B, B' to regulate the flow through the instrument, and are joined by insulated metal tubes, R, R', to the center piece. The taps are fitted at B, B' with adapters to screw into standard-thread 1/8-inch metal tubing connected to the water main (or reservoir) and the waste pipe, respectively. By means of a terminal, T', on the copper tube and a terminal, T, (connected to the platinum rod, through a plug switch, K), wires connect the instrument to a special current-measurer, which may be kept in any convenient position. The current-measurer is graduated according to the use to which the instrument is to be put; for the usual purposes of water treatment it has been found convenient to graduate the scale so that one division represents one part of available chlorine per ten million. The

quantity of water needed for the apparatus is very small; even if it is always kept running though the apparatus, 2 to 4 gallons per hour suffice for its efficient working. The form of instrument of the above sensitiveness will read up to strengths of approximately 5 parts of available chlorine per million, but the manufacturers state that special forms of the instruments can be supplied to measure up to much higher concentrations of chlorine.

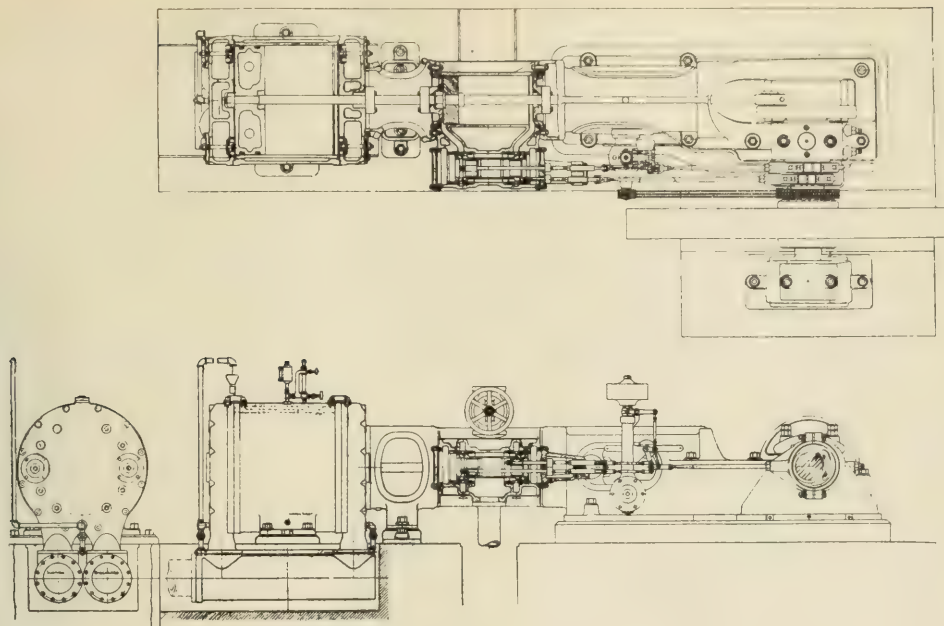


For public water supplies, the instrument may be placed so as to show the quantity of chlorine in a town water-supply as it leaves the waterworks. For sewage effluents, when the chlorometer is placed at the point of discharge of the effluent, it will indicate whether the desirable slight excess of sterilizer is present or not. Water to be used for textile finishing or in laundries is tested just as it enters the tanks. If, however, the chlorometer is to be employed in connection with swimming tanks, it should be attached at the point of efflux.

The instrument is attached on any convenient wall by means of four screws passing through the brass plate. The water to be tested is conveyed by a small pipe which is connected to the apparatus at B. The overflow escaping at B' may be discharged down a waste or returned to the original supply. The rate of flow indicated is obtained by the adjustment of the tap B, the tap B' being fully open. When adjustment is completed, the position of the tap B is allowed to remain stationary, and the water is turned on and off by means of the other tap B', which is always kept closed or fully open. The terminals T and T' are now joined to the current measurer by means of wire, the terminal T being connected with the positive pole. After setting up, water is allowed to flow through the instrument continuously for about 24 hours. Then the tap B' is turned off and is only opened when it is desired to make a reading. To take a measurement of chlorine in a water sample, the plug K is put into position, the tap B' is opened, and when the dial pointer has arrived at a position of equilibrium, the reading on the scale is noted. The action of the chlorometer is based solely upon depolarization and does not depend in any way upon the measurement of the conductivity of the liquid.

THE EFFICIENCY OF CONDENSER AIR PUMPS

In recent years, jet air pumps and rotary air pumps have been introduced for condenser service. The advantages of these types of pumps are as follows: they are simple, practically no attendance is required, and repairs may be easily made. The introduction was facilitated by the shortcomings of the types of reciprocating air pumps in use until lately. These shortcomings consisted in complications such as mechanically operated valves, with the necessary valve gearing, large clearance and flash ports, the necessity for close adjustment on account of the small width of the flash ports, their sensitiveness for entrained water and the fact that at high vacuum the heat of compression warps the mechanically operated valves, and thereby makes further increase of vacuum impossible. Frequently, these



pumps were driven by steam cylinders with complicated Corliss valve gear.

Coupled with these features was the general lack of knowledge of the volumetric efficiency of such pumps. In contradistinction to the ease with which tests can be run on jet and whirling air pumps, tests on reciprocating pumps require more expensive installation and equipment.

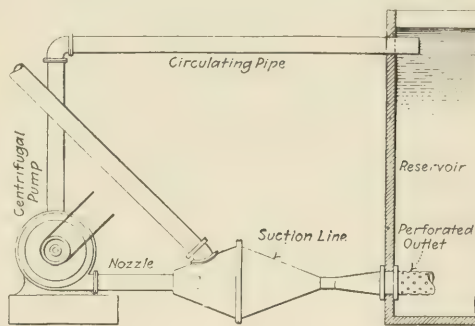
According to the *Industrial World*, 47, No. 16, a new reciprocating pump has been placed on the market by a Pittsburgh firm. This air pump, which is illustrated above, has no mechanically operated valves on the air cylinder, but has instead automatic valves of the multi-ported plate type. There are no flash ports and no large clearance spaces due to such flash ports. It is claimed that the valves require no attention and no oiling; they are said to open and close independent of any adjustment.

The New Mesta Reciprocating Pump was tested for reliability and economy by W. Trinks. His results seem to show that the reciprocating air pump should be used wherever sufficient amount of exhaust steam for feed water heating is available from other sources.

A NEW GAS SCRUBBER

W. R. Heslewood, of Berkeley, Cal., has devised an apparatus for scrubbing flue gases, wherein the scrubbing is effected by water traversing a closed cycle, impelled by a centrifugal pump. The centrifugal pump delivers the water through a nozzle into

a gas case composed of two reducers, bolted together at their large ends and making up the suction line. The water proceeds from the second reducer into an expanding nozzle, from which it is delivered into a tank through a perforated pipe. The centrifugal pump then draws its feed from the same tank. There is suction produced in the gas case by the jet of water, with the result that the flue gases are thereby drawn in, scrubbed and discharged through the holes in the exit pipe. While the



apparatus may be useful for scrubbing out soluble liquids, solids, or gases, it should be determined whether any large amounts of insoluble flue dust would clog the pump and exit holes.

SCIENTIFIC SOCIETIES

PRELIMINARY REPORT FOR THE COMMITTEE ON COAL ANALYSIS OF THE AMERICAN SOCIETY FOR TESTING MATERIALS AND THE AMERICAN CHEMICAL SOCIETY

By W. A. NOYES

INTRODUCTION

Sometime ago committees were appointed by the American Society for Testing Materials and the American Chemical Society for the purpose of revising the standard methods of coal analysis. During the fall of 1911 the two committees were

organized as a joint committee consisting of the following members: W. A. Noyes, *Chairman*, Perry Barker, H. C. Dickinson, A. F. Fieldner, Frank Haas, W. F. Hillebrand, S. W. Parr, S. S. Voorhees, A. H. White.

At the Washington meeting of the American Chemical Society in December, 1911, this committee met and after a careful discussion of the problems to be considered appointed the following sub-committees:

1. Preparation of samples, including loss of moisture in

sampling—Mr. Fieldner, *Chairman*, Haas, Hillebrand, Voorhees, Parr and Barker.

2. Moisture—Dr. Hillebrand, *Chairman*, Fieldner, Parr.

3. Deterioration—Professor Parr, *Chairman*, Fieldner, Haas, Dickinson.

4. Volatile Matter—Professor Parr, *Chairman*, Fieldner, Haas, Dickinson.

5. Fixed Carbon and Ash Professor Parr, *Chairman*, Fieldner, Hillebrand.

6. Sulfur—Mr. Barker, *Chairman*, Voorhees, Dickinson.

7. Phosphorus—Dr. Hillebrand.

8. Ultimate Analysis—Mr. Fieldner, *Chairman*, Parr, White.

9. Calorimetric Determination—Mr. Dickinson, *Chairman*, Haas, Barker.

10. Interpretation and Computation—Whole Committee.

These sub-committees have been actively at work and at the Milwaukee meeting in March it was decided to publish at the present time a preliminary report of the work of each sub-committee, which it is hoped will furnish the basis for discussion on the part of members of the committee and of others who are interested in the matter, to the end that it may be possible at the Rochester meeting in September to carry the discussion far enough to make it possible to present a final report in the near future. The reports of the sub-committees, which are given below, are in all cases the results of a considerable amount of correspondence and discussion, but it is to be clearly understood that these recommendations are not final and have not been endorsed by the committee as a whole, and indeed in several cases it has not been possible to carry the discussion far enough so that it can be said that the report represents fully the sentiment of the sub-committee. In other words the chairmen are primarily responsible for these reports in their present form.

Every one interested in the subject of coal analysis is earnestly urged to read these reports and to send to the chairman any suggestions which he thinks may be of value to our committee. As an introduction to these reports the following items, which are partly the result of the discussion at Milwaukee, may be mentioned:

It can not be emphasized too strongly that in coal we have an extremely complex mixture of organic compounds, many of which are easily changed by oxidation and otherwise by exposure to the air, and containing water in such condition that a part of it is usually lost with the greatest ease, while the material after complete drying is excessively hygroscopic, probably even more so than calcium chloride. These actual conditions give rise to variations in analysis very far beyond those which most analysts, who have not studied the matter carefully, realize. It has seemed necessary, therefore, to the committee to place rather liberal estimates on the allowable variations in the analysis, and in addition to this we wish to impress it upon every analyst that it is necessary for him to convince himself by personal experiment (1) *that the variations in his own method of procedure do not cause errors greater than the allowable amount, and* (2) *if possible, that the methods give results which will agree with those of other analysts.*

Sampling.—A committee of The Society for Testing Materials on coal specifications, of which Mr. J. A. Holmes, of the Bureau of Mines, Washington, is chairman, has charge of the questions relating to the sampling of coal under different conditions, in the mine, on cars, in bins, etc. By mutual agreement that committee considers all questions up to the point of furnishing to the laboratory a five-pound sample, which our committee think should be of one-eighth inch size and which, of course, must be submitted in a sealed can under conditions to prevent loss of moisture and deterioration. It was the consensus of opinion at Milwaukee that in the preparation of this five-pound sample at least fifty pounds of coal should be crushed to one-

eighth inch size by a suitable mill. A mill which is suitable for this purpose is sold at a price of \$7.50 by the Enterprise Manufacturing Company, Philadelphia. In sampling and analyzing it is necessary to emphasize again the fact that coal is an extremely changeable substance, that all operations should be carried out as rapidly as possible, and that the analysis should be made as soon as practicable after the sample reaches the laboratory.

Moisture.—It is probably impossible to secure an actually exact determination of the amount of moisture present in coals, especially in those of the bituminous or lignite type, partly because some compounds in the coal decompose readily with loss of water, and partly because of the rather rapid oxidation of such coals when heated in the air. The determination of moisture is, therefore, to be considered as empirical rather than theoretical, and we should strive at conditions that should give concordant results, the agreement of different analysts being of more importance than a determination of the actual amount of moisture in the coal, since the calorific value of the "pure coal" depends on the method of determining moisture in such a manner that it is unimportant whether some of the moisture is counted as moisture or as a part of the coal.

Volatile Matter.—The determination of volatile matter is empirical even to a much greater extent than that of moisture, and here again the point that must be aimed at is to secure conditions which can be accurately reproduced by different analysts. The most important change which seems necessary from the procedure recommended by the committee of the American Chemical Society in 1899 is the application of a gentle heat at first to those lignites which undergo a large mechanical loss if the full heat is applied at once.

Ash.—Practically it is expected that for the present, at least, the ash which will be reported by coal analysts will be that which is found by careful burning of the coal at a temperature finally reaching about 700–750° C. Theoretically, however, the ash should include all substances in the coal other than moisture and organic compounds which are combustible. It seems desirable, therefore, to introduce as a basis for careful work, especially for the calculations of engineers, a "corrected ash" which would include iron pyrites, sulfur, calcium carbonate, calcium sulfate, ferrous sulfate and the water of hydration of clayey matters which is not expelled at 110°.

Calorimetric Determination.—As brought out by Mr. Fieldner, under conditions of actual practice coals are always burned in such a manner that the water escapes as vapor. It is probably not possible at once and perhaps not soon to induce engineers to change their practice of basing their calculations on the calorific value of coals burned to liquid water, but we think that in all cases in the future the statement of calorific values should have appended to it either the words "liquid water" or "vapor of water at 20°."

In conclusion, I wish to express our thanks to many chemists not members of our committee who have cooperated with us and participated in our discussions, especially to H. C. Adams, Horace C. Porter, W. H. Blauvelt, J. D. Davis, William Brady, W. B. Wiley, L. A. Touzalin and A. C. Parsons.

PREPARATION OF LABORATORY SAMPLES

By A. C. FIELDNER, *Chairman*

AMOUNT AND FINENESS OF SAMPLE FOR TRANSMITTAL TO THE LABORATORY

Assuming thorough mixture, accuracy in the reduction of gross samples to a convenient quantity for transmittal to the laboratory, is largely dependent on crushing the extraneous impurities of slate, pyrite, etc., to such a degree of fineness before each process of mixing and dividing, that the inclusion of a few pieces more or less in the various divisions can not materially change the character of the final sample.

That there should be a nearly constant ratio between the largest particle of heaviest impurity and the weight of sample, in the various stages of reduction is essential, otherwise excessive errors are introduced at the particular point in the process where this ratio is exceeded. Hence the quantity of sample to send to the chemist will be governed by the relative proportion of free impurities and the practical limits of fineness to which these impurities can be crushed at the point of sampling.

Bailey¹ places the following limits beyond which samples should not be divided when crushed to different sizes:

Size of impurities	Minimum weight of sample
2-mesh.....	8300 grams (18.3 lbs.)
4-mesh.....	1100 grams (2.5 lbs.)
8-mesh.....	120 grams

This table is based on a ratio of 0.02 per cent between the weight of the largest pieces of slate and the minimum weight of sample. For the above limits of reduction in the case of samples containing 5 per cent ash as free impurities, Bailey computes the probable error in ash at 0.20 per cent and the maximum possible error occurring once in 10,000 times at 1.00 per cent ash.

Somermeier² gives the following table as a guide in selecting and reducing samples containing pieces of pyrite equivalent to cubes of different sizes:

Size in inches	Weight of sample	
	Grams	oz. or lbs.
1/64.....	1	1/28 ounce
1/32.....	8	2 7/8 ounce
1/16.....	64	2 2/7 ounces
1/8.....	510	1 1/8 pounds
3/16(a).....	1700	3 3/4 pounds
1/4(a).....	2090	4 3/5 pounds
1/2.....	4090	9 pounds
3/4.....	13700	30 pounds
1.....	32700	72 pounds

(a) Interpolated by the writer. Size of openings in 4-mesh sieves vary from 3/16 inch to 1/2 inch, depending on thickness of the wire.

The above table is based on a ratio of 0.019 per cent between the weight of ash resulting from the largest particle of pyrite and the weight of sample.

This ratio according to Somermeier is sufficiently small to keep the error in ash less than 0.5 per cent, provided the sample is thoroughly mixed and properly reduced.

The results of a considerable number of sampling experiments made by the Bureau of Mines indicate that the quantities of sample given in the above table for various sizes of particles are none too large.

The sub-committee, therefore, recommends the following minimum weight of sample for transmittal to the laboratory.

Size of largest impurities	Minimum weight of sample
1/2 inch.....	75 pounds
3/4 inch.....	30 pounds
1/4 inch.....	9 pounds
3/16 to 1/2 inch (a) (4-mesh).....	5 pounds
1/8 inch.....	3 to 5 pounds

(a) The usual 4-mesh screen has openings of 3/16 inch to 1/2 inch in length.

SPECIAL MOISTURE SAMPLES

Unless special crushing and sampling apparatus is available, much moisture is lost during the reduction of the gross sample to the smaller sizes given above. Therefore, when the moisture content is important, a special moisture sample should be accumulated by placing in a hermetically sealed receptacle small parts of the freshly taken increments of the gross sample.³

¹ "Accuracy in Sampling Coal," by E. G. Bailey, *THIS JOURNAL*, **1**, 176 (1909).

² "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 67, McGraw Hill Book Co. (1912).

³ See page 29, *Bull. 63*, Bureau of Mines, "Sampling Coal Deliveries," by G. S. Pope (1913).

These parts should be broken to about 1/2 inch size as accumulated. If possible, the mixing should be done in the closed receptacle, and an average sample of about 3 pounds quickly transferred to a moisture-tight container for shipment to the laboratory.

Mine samples when reduced in the mine do not require a special moisture sample, owing to the usual high humidity of mine atmospheres.

CONTAINERS FOR SHIPMENT TO LABORATORY

Samples in which the moisture content is important should always be shipped in moisture-tight containers. A galvanized iron or tin can with a screw top which is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit.

Samples in which the moisture content is of no importance need no especial protection from loss of moisture.

PREPARATION OF LABORATORY SAMPLES

The method of preparing a suitable sample for the various analytical determinations that are required in coal analysis must conform as nearly as practicable to the following requirements:

(1) A uniform distribution of coal and impurities must be maintained throughout the process of reducing to the final powdered sample. This should be insured by thorough mixing between each dividing or quartering process, and by having due regard to the ratio of size of largest impurities and weight of sample as given in the preceding tables.

(2) Changes in moisture during the procedure of sampling must be reduced to a minimum.

Coal, especially when in a pulverized condition, is exceedingly susceptible to change in moisture content. The general tendency is loss of moisture on dividing to finer sizes. This may amount to several per cent in coal that has not been previously air-dried.

The equilibrium point of the moisture in pulverized coal varies with the temperature and humidity of the air. Coal that has reached equilibrium with respect to moisture in an atmosphere of low humidity will reabsorb moisture if placed in an atmosphere of higher humidity.¹ Hence to reduce the loss of moisture to a minimum the sample received by the laboratory should be brought to an approximately air-dry condition, before it is pulverized and reduced to the final sample for analysis. Furthermore, the unavoidable exposure of the sample to the air of the sampling room both before and after the air-drying period must be limited to the shortest possible time. The use of an air-tight grinding apparatus such as the ball mill is essential for the final pulverization.

The results² of a considerable number of experiments comparing the ball mill and bucking board at the United States Fuel Testing Plant show that air-dried samples rubbed down on a bucking board may gain or lose moisture, depending on the extent of previous air-drying and the humidity conditions of the sampling room.

If the sample has not been air-dried, or if a ball mill is not available, a special moisture sample should be taken after the coal has been rapidly reduced to 10- or 20-mesh size. The main portion of the sample may then be pulverized and reduced by any suitable apparatus without regard to further moisture changes. The sample obtained by this method will be more susceptible to loss of moisture while weighing out portions for analysis, than air-dried samples. The moisture must, of course, be accurately determined in both samples to bring the calculations to the same wet or dry basis.

¹ For experimental data on moisture changes in coal samples, see *Bull. 28*, Bureau of Mines, "Experimental Work of the Chemical Laboratory," by N. W. Lord.

² "Experimental Work of the Chemical Laboratory," by N. W. Lord, *Bull. 28*, Bureau of Mines, and *Bull. 323*, U. S. Geological Survey.

(3) Due regard must be given to the tendency of coal to absorb oxygen and deteriorate in heating value.

That appreciable quantities of oxygen are absorbed during prolonged air-drying at 35° C. is shown by the following experimental results obtained by H. C. Porter, of the Bureau of Mines.

OXYGEN¹ ABSORBED BY 100 GRAMS OF COARSELY CRUSHED COAL (AS RECEIVED) ON EXPOSURE TO AIR AT 35° C., REPLENISHING THE OXYGEN OF THE AIR INTERMITTENTLY AS ABSORBED

Days	Fresh mine sample of bituminous coal from Pittsburgh bed. Air-drying loss (usual method) = 2.5 per cent		Fresh mine sample of sub-bituminous coal from Wyoming. Air-drying loss (usual method) = 14.2 per cent	
	Cc. oxygen absorbed (0° C. and 760 mm.)	Percentages by weight of oxygen absorbed	Cc. oxygen absorbed (0° C. and 760 mm.)	Percentage by weight of oxygen absorbed
1.....	43	0.06	81	0.12
2.....	71	0.10	155	0.22
3.....	71	0.10	204	0.29
4.....	87	0.13	264	0.38
5.....	100	0.14	312	0.45
6.....	109
7.....	377	0.54
8.....	123	..	419	..
Correction(a).....	6	—	64	—
8.....	117	0.17	483	0.70

(a) Based on analysis of air in container, before and after.

MOISTURE REMOVED DURING TEST

Pittsburgh coal.....	2.46 per cent
Wyoming coal.....	5.27 per cent

"The coal in the above tests was used in the condition as received from the mine sampler, having been crushed by him so as to pass through a 2-mesh screen. The sample was mailed to the laboratory in a galvanized iron can, sealed moisture-tight.

"There are two sources of error in these tests, both of which tend to lessen the oxygen absorption: (1) the coal was in a confined space with no circulation of air, so that the moisture vapor arising from the coal was not displaced by air as readily as in the usual air-drying process; and (2) the normal oxygen content of the air was not maintained constantly, the supply of fresh oxygen being admitted only once in 24 hours.

"The results show, however, that the oxidation error during air-drying at 35° C. may amount in the case of a sub-bituminous coal to at least 0.4 per cent in 4 days and 0.7 per cent in 8 days. The calorific values determined on such an air-dried sample will be in error to a somewhat larger extent, owing to the neutralizing effect of oxygen on the hydrogen and carbon of the coal."

Mine samples of coal crushed to 4 mesh ($\frac{3}{16}$ inch to $\frac{1}{8}$ inch) and spread out to a depth not exceeding 1 inch, in circulating air at 10° C. above room temperature will become approximately air-dry in the following periods of time:

Appalachian coals.....	8 to 24 hours
Illinois and similar coals.....	12 to 48 hours
Sub-bituminous coals and lignites.....	48 to 72 hours

Lignites and some sub-bituminous coals continue to lose moisture over longer periods of time than given above; however, in view of Porter's experiments, the above maximum limits should not be exceeded.

METHODS OF SAMPLING RECOMMENDED BY THE SUB-COMMITTEE

The following alternate methods of preparing laboratory coal samples are recommended as conforming to the theoretical requirements set forth in the preceding paragraphs, and as being commercially practicable for technical coal analysis.

METHOD I

Samples of coal received by the laboratory which exceed 5

¹ Quoted from private communication from H. C. Porter.

pounds in weight, or 4 mesh (length of openings in sieve not to exceed 0.20 inch) in size should be rapidly crushed to 4 mesh, mixed and reduced to not less than 5 pounds. This portion is then transferred to a weighed sheet-metal pan, spread out to a depth of 1 inch and at once weighed. The pan is placed in a special drier² and the coal allowed to air-dry in circulating air at 10° C. to 15° C. above the sampling room temperature, until the rate of moisture loss is less than 0.1 per cent per hour, as shown by two weighings made at intervals of 2 to 4 hours. The time limits already given in this report should not be exceeded. In most cases bituminous coal and anthracite will be air-dry if left in the drier over night.

Immediately after the last weighing has been made, the entire sample should be rapidly pulverized to 10-mesh size, mixed and reduced to 500 grams with an enclosed riffle sampler³ whose sub-divisions are not more than $\frac{1}{2}$ inch apart. This 500-gram portion is at once transferred to the porcelain jar (8.95 in diameter and 9.65 inch high) of an Abbé ball mill, sealed air-tight and pulverized to 60-mesh. Bituminous coals require about $\frac{1}{2}$ hour and anthracites about 2 hours to pulverize to 60 mesh.

The jar should contain about one-third of its volume of 1-inch, well rounded flint pebbles, and should be rotated at about 60 revolutions per minute. The coal is removed from the porcelain jar by emptying the contents on a $\frac{1}{2}$ inch screen, which is vigorously shaken a moment to detach the coal from the pebbles. The sample is then reduced to the final laboratory sample of approximately 60 grams by successively halving it with a small, enclosed riffle sampler. All of the final sample should then be put through the 60-mesh sieve, and at once transferred to a 4-ounce wide-mouthed bottle which is securely closed with a well fitting rubber stopper. To avoid moisture change the sieve should be covered while sifting. Usually a few particles of coarse material remain on the sieve. These must be rubbed down on a bucking board or mortar to 60-mesh, and thoroughly mixed with the sample. (If one could be certain that all of each sample would pass the 60-mesh sieve it would be preferable to omit sieving, since it has a tendency to segregate the particles of slate and pyrite and offers an opportunity for change in moisture content. On the other hand, if the sieving is omitted there is great danger of rather coarse particles of slate and pyrite being present in the final sample.) The mixing and reducing of the sample after removal from the ball mill should be done rapidly to minimize loss or absorption of moisture. The total time elapsing from the opening of the ball-mill jar to the stoppering of the laboratory sample bottle need not exceed two or three minutes.

The total loss in weight of samples while air-drying is reported as air-drying loss

METHOD II

Samples of coal if larger than 4-mesh (0.20 inch) should be rapidly reduced to 5 pounds at 4-mesh or finer as in Method I.

This 5-pound portion is quickly passed through a suitable crushing apparatus—rolls or enclosed coffee mill type of grinder, adjusted to crush to 10- or 20-mesh size. A 60-gram moisture sample should be taken, without sieving, immediately after the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the 10- or 20-mesh product, and should be placed directly in a rubber-stoppered bottle.

¹ For details of air-drying oven see *Bull.* 9, 4th series, Ohio Geological Survey, "Coal," by Bownocker, Lord and Somermeier (1908), page 312, or *Technical Paper* 8, Bureau of Mines, "Methods of Analyzing Coal and Coke," by F. M. Stanton and A. C. Fieldner (1912), page 4, or "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 71, McGraw-Hill Book Co. (1912).

² For details of riffle sampler see *Bull.* 9, 4th series, Ohio Geological Survey, page 313, or "Coal, Its Composition, Analysis, Utilization and Valuation," by E. E. Somermeier, page 73.

The main portion of the sample is further pulverized until all passes through a 20-mesh sieve. It is then thoroughly mixed and reduced on the riffle to about 120 grams, which is pulverized to 60-mesh by any suitable apparatus without regard to loss of moisture. After this sample has been passed through the 60-mesh sieve it is again mixed and divided on a small riffle to 60 grams. The final sample should be transferred to a 4-oz. rubber-stoppered bottle.

Coal containing visible superficial moisture should be spread out in weighed pans and allowed to air-dry as in Method I, or at room temperature, otherwise considerable loss of moisture will take place while crushing to 10-mesh size. The percentage of loss in weight is recorded and the analysis of the air-dried sample corrected to the "as received" basis.

Notes on Method I.—(1) This method of preparing coal samples was developed by Lord and Sommermeier at the Fuel Testing Plant of the U. S. Geological Survey at St. Louis. It has been used for several years by the Bureau of Mines in connection with the analysis of mine samples of coal, where especial consideration must be given to loss of moisture during the sampling process. The Bureau of Mines uses a chipmunk jaw crusher for crushing the sample received at the laboratory to 4-mesh size, and a Sturtevant roll crusher for reducing the 4-mesh material to 10- or 20-mesh size. The rolls have one disadvantage, in that with some coals, flakes are formed which must be broken up by rubbing through a sieve before the sample can be reduced on the riffle. On the other hand, the rolls have a large capacity and are easily cleaned.

Coffee or bone mill types of grinders may be used for grinding to 10- or 20-mesh size. They should be entirely enclosed and provided with a covered hopper and receptacle of sufficient capacity to hold the entire 5-pound sample.

(2) A new porcelain jar ball mill and pebbles should always be tested for abrasion before use. This may be done by grinding 500 grams of sugar for a period of 2 hours, and then determining the ash in the sugar; or by keeping a record of the loss in weight of jar and pebbles and the weight of coal ground. No trouble has ever been experienced by the Bureau of Mines in the use of the ball mill.¹

(3) A large number of duplicate sampling experiments by Method I, beginning with a 3- to 5-pound 4-mesh sample have

A COMPARISON OF TOTAL MOISTURE IN DUPLICATE SAMPLES OF COAL

DESCRIPTION OF COAL	Sample no.	TOTAL MOISTURE			
		Sampled by Method I	Sampled by Method II	Per cent	Difference
Bituminous, Pittsburgh bed, dry	10	1.99	1.74	—0.25	
Bituminous, Pittsburgh bed, dry	11	1.97	1.76	—0.21	
Bituminous, Pittsburgh bed, dry	12	1.97	1.74	—0.23	
Bituminous, Pittsburgh bed, wet	13	3.46	2.92	—0.54	
Bituminous, Pittsburgh bed, wet	14	3.62	2.74	—0.88	
Bituminous, Pittsburgh bed, wet	15	3.55	2.84	—0.71	
Bituminous, Pittsburgh bed, dry	16	2.80	2.58	—0.22	
Bituminous, Pittsburgh bed, dry	17	2.67	2.56	—0.11	
Bituminous, Pittsburgh bed, dry	18	2.81	2.57	—0.24	
Sub-bituminous, Wyoming, dry	19	15.99	15.56	—0.43	
Sub-bituminous, Wyoming, dry	20	16.21	15.61	—0.60	
Sub-bituminous, Wyoming, dry	21	15.89	15.62	—0.27	

been made by the Bureau of Mines on a wide range of coals. The variations in moisture usually range from 0 to 0.20 per cent and the variations in ash from 0 to 0.4 per cent.

Notes on Method II.—(1) This method requires less special apparatus (such as air-drier, and ball mills) than Method I, and, therefore, can be more readily adapted to the apparatus at hand in the ordinary analytical laboratory. The sample can be prepared for analysis in a much shorter time than by Method I.

¹ For experimental data on abrasion in ball mills see paper on "Accuracy and Limitations of Coal Analysis," by A. C. Fieldner, *THIS JOURNAL*, 5, 281 (1913).

The moisture obtained by this method is usually somewhat lower than by Method I, as shown in the preceding table of experimental results obtained on duplicate samples analyzed by Methods I and II.

(2) The Bureau of Mines has used this method during a period of several years in the Fuel Inspection Laboratory at Washington. The samples as received, if larger than $\frac{1}{4}$ inch, are first pulverized with a jaw crusher to about $\frac{1}{8}$ inch and then by a roll crusher to 20 mesh. A planetary disk grinder is used for pulverizing to 60 mesh. This machine, on account of heating, can not be used for anthracite.

Duplicate samples almost invariably check within 0.4 per cent in ash.

(3) For crushing samples in the field S. W. Parr recommends a small portable mill which will reduce the samples to $\frac{1}{8}$ inch size before quartering.

(4) S. W. Parr and W. A. Noyes recommend that all samples should be crushed to $\frac{1}{8}$ inch size in the field and reduced to not less than five pounds before transmittal to the laboratory.

(5) The size to which the final laboratory sample should be pulverized is best indicated by showing the deviation in ash and sulfur that is caused by one particle more or less of cubes of pyrite equivalent to the openings in the various sizes of sieves.

Nominal size of sieve	Length of opening mm.	Weight of pyrite cube equivalent to opening Gram	Weight of sulfur in this cube Gram	Weight of ash produced from this cube Gram
40 mesh	0.42	0.00037	0.00019	0.00024
60 mesh	0.34	0.00020	0.00011	0.00013
80 mesh	0.23	0.00006	0.00003	0.00004

An inspection of the above table shows that 40 mesh is obviously too coarse to insure satisfactory duplication, inasmuch as a deviation of only 10 particles of pyrite in the 1-gram sample would cause a difference of 0.19 per cent sulfur and 0.24 per cent ash. Even 60 mesh is scarcely fine enough for high-sulfur coals. In such cases 80 mesh would be preferable.

MOISTURE

By W. F. HILLEBRAND, *Chairman*

In view of our own experience and that of the chemists who cooperated with a subcommittee of the International Committee on Analyses¹ it seems needless to strive at present in ordinary work for a very high degree of refinement in the determination of moisture. So sensitive are coals to humidity changes of the air that it is evidently only by chance that two or more analysts will reach the same results for moisture in a given coal, especially if they live in different cities or make the tests on different days in the same place. To the truth of this the report of the above-mentioned International Committee bears abundant testimony. The variations therein shown are probably due, in part to lack of realization on the part of many of the analysts of the magnitude of the changes in moisture content that may arise during the transfer of the coal from the containing vessel to the drying receptacle and during the weighing operation. Nevertheless, the chances of variation are so serious that the opening statement above is fully justified.

A. APPROXIMATE METHOD

Use a pair of shallow weighing capsules with ground caps or other well-fitting covers. Suitable forms are indicated below. Heat these under the conditions at which the coal is to be dried, stopper or cover, cool over concentrated sulfuric acid for 30 minutes and weigh.

Dip out with a spoon or spatula from the container two portions of coal of about 1 gram weight each, put these quickly into the drying vessels, close, and weigh at once.

¹ *Proceedings 8th Intern. Congr. Appl. Chem.*, 25, 41.

An alternative procedure (more open to error), after transferring an amount slightly in excess of 1 gram, is to bring to exactly 1 gram weight (± 0.5 mg.) by quickly removing the excess weight of coal with a spatula. The utmost dispatch must be used in order to minimize the exposure of the coal until the weight is found.

Further procedure:

(a) *For Anthracite and Bituminous Coals*

Quickly place the vessels open in a preheated oven (at $104-110^{\circ}$ C.) through which passes a current of air dried by concentrated sulfuric acid. Close the oven at once and heat for one hour. Then open the oven, cover the capsules quickly and place in a desiccator over concentrated sulfuric acid. When cool, weigh.

(b) *For Sub-bituminous and Lignitic Coals*

Instead of air use a current of dry carbon dioxide, both for the preliminary heating of the capsules as well as for the drying of the coal. After the hour's heating, open the oven, cover the capsules and place them in a vacuum desiccator over concentrated sulfuric acid. Exhaust the desiccator to remove the carbon dioxide from the capsules. When cool, slowly let in dry air and weigh at once.

Notes on Method A.—(1) Although watch glasses ground to fit, and with clamp, are most effective drying vessels on account of their shallowness, it is probable that glass capsules as used by S. W. Parr and as recommended by the International Committee will be found most convenient. The capsules themselves should be about $2\frac{1}{2}$ cm. wide and $1\frac{1}{2}$ cm. deep. The shallower they are, consistent with convenient handling, the quicker and more perfect the drying. The Parr capsules have the upper part of the wall ground on the outside and the cap is ground on the inside, leaving a smooth edge, a feature which facilitates transfer of the coal to the ashing vessel.

A porcelain cup (Eimer and Amend, No. 2657) is preferred at the Bureau of Mines, where it is used with a well fitting aluminum cover. It has the disadvantage of greater depth as compared with the glass capsule, but if demand arose this defect could be remedied. Its only advantage over the glass capsule lies in permitting the ash determination to be made on the moisture sample without transfer.

(2) The oven must be so constructed as to have a uniform temperature in all parts and a minimum of air space. The air current must be rapid enough to renew the gas in the oven frequently when the oven holds from 6–12 vessels of coal.

The cylindrical form of oven shown in *Technologic Paper 8*, of the Bureau of Mines, p. 5, and holding 6 crucibles, is well adapted for the purpose; also a new rectangular oven of the same Bureau, holding 12 crucibles and measuring inside $1\frac{1}{2}$ inches high by 4 inches wide and $14\frac{1}{2}$ inches long. The approximate air space in each of these ovens is 0.05 cubic foot. With this type of oven, of small air space, it has been found at the Bureau of Mines that the air must be renewed from 2 to 4 times a minute to obtain the maximum loss in weight from the coal in 1 hour.

S. W. Parr uses an oven 12 inches in each of the three directions, and here the renewal of air need not be so rapid, 8 to 10 times in an hour being probably sufficient.

(3) Although carbon dioxide is absorbed by coal at room temperature there is no absorption above 100° C. The need for modifying the procedure for sub-bituminous and lignitic coals arises from the fact that such coals undergo very many times the amount of oxidation that Appalachian coals suffer. Nitrogen gas is to be preferred to carbon dioxide because its density is so near that of air that it will be unnecessary to displace it from the capsules before final weighing. If this gas is used, a vacuum desiccator is unnecessary.

(4) The International Committee in its report recommends,

when using air, to remove one of the capsules from the oven at the expiration of 30 minutes, to continue heating the other for 30 minutes longer, and to accept the higher loss in weight, if a difference is shown, as may happen with certain coals. Our committee has not deemed it advisable to adopt this precaution, both on account of the added labor involved in testing four portions of a sample instead of two and because the probable error in the determination of the true moisture content is so large as to render the precaution of doubtful value.

B. METHODS OF GREATEST ACCURACY

(1) Heat as in Method A, but in a current of dry nitrogen that is free from oxygen. Instead of a shallow vessel a U-tube with well ground stoppers may be used, which tube can be hung in an oven at the temperature of $104-110^{\circ}$. Fill the tube with nitrogen before taking its weight empty, and weigh always with a counterpoise tube of about the same displacement and weight. Introduce about a gram of the coal quickly through a short and wide-stem funnel without attempt to secure a weight of exactly 1 gram. Before hanging the tube in the preheated oven pass nitrogen to displace all air, and continuously while heating. When the last trace of moisture has disappeared from the outlet of the tube, remove from the oven and let cool with the gas still passing. When cool close the cocks, hang in the balance case for 15 minutes and after opening one cock weigh with the counterpoise. The counterpoise need not be filled with nitrogen.

As a check the water given off may be collected in sulfuric acid and weighed, care being taken to keep the absorption vessel full of nitrogen. The weight of water thus obtained is a little higher than that found indirectly.

BA. ALTERNATIVE METHOD (FOR USE WHEN TIME DOES NOT PRESS)

Dry in a vacuum desiccator over sulfuric acid of maximum concentration for 3 and 7 days, longer if necessary.

The vacuum should be high—not over 3 millimeters of mercury pressure—and should be checked by a manometer. The capsules mentioned above may be used. Before evacuating fill the desiccator with an inert gas, and before opening the desiccator carefully let in air dried by sulfuric acid. Weigh immediately.

This method is easy of execution and is sound in principle since a possible error due to loss of gaseous constituents is negligible.

It has not been deemed advisable to recommend the xylene method of Constam (boiling a large weight of coal with xylene and collecting and measuring the water that distills over) since, though promising, the method has not been subjected to exhaustive test.

ALLOWABLE VARIATIONS

	Same analyst Per cent	Different analysts Per cent
Moisture under 5 per cent.....	0.2	0.3
Moisture over 5 per cent.....	0.3	0.5

VOLATILE MATTER

By S. W. PARR, Chairman

It is recommended that for volatile matter determinations a 10-gram platinum crucible be used having a capsule cover, that is, one which fits inside of the crucible and not on top. The crucible with one gram of coal is placed in a muffle maintained at approximately 950° C. for 7 minutes. With a muffle of the horizontal type, the crucible should not rest on the floor of the muffle but should be supported on a platinum or nichrome triangle bent into a tripod form. After the more rapid discharge of the volatile matter, well shown by the disappearance of the luminous flame, the cover should be tapped lightly to

more perfectly seal the cover and thus guard against the admission of air.

ALTERNATE METHOD

One gram of coal is placed in a platinum crucible of approximately 20 cc. capacity (35 mm. in diameter at the top and 35 mm. high). The crucible should have a capsule cover which will readily adjust itself to the inside upper surface of the crucible. The crucible is placed in the flame of a Meker burner, size No. 4, having approximately an outside diameter at the top of 25 mm. and giving a flame not less than 15 cm. high. The temperature should be from 900° to 950° C. determined by placing a thermocouple through the perforated cover which for this purpose may be of nickel. The junction of the couple should be placed in contact with the center of the bottom of the crucible. Or the temperature may be indicated by the fusion of pure potassium chromate in the covered crucible (fusion of K_2CrO_4 , 940° C.). The crucible is placed in the flame about 1 cm. above the top of the burner and the heating is continued for 7 minutes. After the main part of the gases have been discharged the cover should be tapped into place as above described.

For lignites a preliminary heating of 5 minutes is carried out, during which time the flame of the burner is played upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating the crucible is placed in the full burner flame for 7 minutes as above described.

ALLOWABLE VARIATIONS

	Same analyst Per cent	Different analysts Per cent
Bituminous coals.....	0.5	1.0
Lignites.....	1.0	2.0

DETERMINATION OF ASH

By S. W. PARR, *Chairman*

In any outline for the determination of ash the attempt must be made to meet the conditions of the widely varying mineral constituents of coals. Those of the Illinois type perhaps have disturbing constituents in greatest amount. These are (a) calcium carbonate, (b) iron sulfate, (c) iron pyrites.

Concerning the extent to which carbonates are present, out of 500 samples of Illinois coal examined, only 9 per cent were found to have calcium carbonate present in an amount less than 0.2 per cent. Very nearly half of the samples have this constituent in excess of 1 per cent. One-fifth of the samples have more than 2 per cent of calcium carbonate and a very considerable number were found to have over 4 per cent with a few isolated cases reaching as high as 10 per cent of calcium carbonate in the raw coal.

Concerning the distribution of sulfate, investigations show this constituent practically always present and in the form of ferrous or ferric sulfate. In the fresh coal the amount varies from a few tenths up to 1 per cent. There is a rapid increase in the content of sulfate in the laboratory sample ground to 60 mesh. In a large number of cases examined, the amount of this constituent had doubled during six months of laboratory storage. An examination of the samples which had been retained in storage in the buckwheat size without fine grinding showed that the increase in sulfate was practically confined to the finely divided particles; that is to say, in that part of the sample which will pass a 60-mesh screen practically all of the increase in sulfate is found. That part of the sample which is retained on a 20-mesh and which passes through a 10-mesh has very little if any increase in sulfate, and the next larger size has so little increase that it may be considered as having the normal content as found in the vein sample.

As to sulfur in the form of sulfide it must be looked upon as an additional element of disturbance in the presence of cal-

cium carbonate, for the reason that any temperature adequate for burning off of carbon will result in the burning also of the sulfur to sulfur dioxide and part or all of the calcium carbonate to calcium oxide. Under these conditions calcium sulfate is inevitably formed. If this reaction were complete or definite in amount, the proposition would be much simplified. An additional point to be observed is the fact that calcium oxide may further increase in weight from absorption of sulfur from the gas flame.

In the final method for ash determination the following items should be borne in mind.

First, Calcium carbonate begins rapid decomposition at and above 900°; below that temperature the decomposition is partial but evident at temperatures above 600° C., or a dull red, and must be considered.

Second, Calcium oxide in the presence of iron pyrites readily takes up sulfur and retains the same in the form of calcium sulfate. Attention should be called in this connection also to the fact that where calcium oxide is present the sulfur from the gas flame may be readily absorbed, with the formation of calcium sulfate.

Third, If high temperatures are maintained during the process of burning off the carbon the quantity of sulfate is seriously modified by reduction in the presence of red-hot carbon.

Fourth, Temperatures which are carried to the fusion point will further modify normal constituents by the formation of calcium silicate and the liberation of sulfur trioxide.

Fifth, Ferric sulfate is decomposed at 550 to 600° C. and ferric sulfate at 700° C. With the temperature necessary for burning off the carbon there is likely to be a transfer of sulfur trioxide to the calcium oxide. The decomposition of calcium sulfate does not occur rapidly below 1100° C. in the absence of carbon, but may occur to a disturbing extent at 900° C. or above.

Sixth, Sulfur in the form of iron pyrites is completely oxidized at the low temperatures indicated, along with the burning out of the carbon. If it is so discharged it does not operate to disturb the values by uniting with calcite, but in so far as calcium oxide develops, it is retained.

METHOD FOR DETERMINING ASH

Unless the coal is of a type known to be free from carbonates the amount of carbon dioxide must be determined. A five-gram sample, recently boiled distilled water and dilute hydrochloric acid are employed, making use of any convenient apparatus for collecting, absorbing and measuring accurately the carbon dioxide discharged from the coal. It is most convenient to obtain the factor as in the form of carbon.

One gram of coal, either freshly weighed or that which has been used for the moisture determination, is ignited in a shallow capsule or porcelain crucible by placing directly in a muffle maintained at a dull or cherry-red temperature between 700 and 750° C. and retained at this temperature for 20 or 30 minutes or until all of the carbon is burned out. The capsule is cooled in a desiccator and weighed. In the absence of a muffle the desired temperature may be obtained by placing the capsule at first just above the tip of a Bunsen flame turned down to about 2 or 3 inches in height. After the larger part of the carbon is burned off in this manner the flame is increased so that the tip comes well into contact with the bottom of the capsule.

For coals having carbon dioxide present in an amount to exceed 0.2 per cent, the ash after cooling is moistened with a few drops of sulfuric acid (diluted 1 : 1) and again carefully brought up to 750° C. and retained at that temperature for 3 to 5 minutes. The capsule is cooled in a desiccator and weighed. Three times the equivalent of carbon present as carbon dioxide is subtracted from the ash as weighed in order to restore the weight of the calcium sulfate formed to the equivalent of calcium carbonate.

A full discussion of the determination of ash will be published soon.

CORRECTED ASH

The application of a correction for sulfur present in the iron pyrites depends largely upon the use to be made of the results. For technical purposes it may well be omitted. For comparative purposes, especially where use is to be made of the pure coal or unit values, it should be applied. Five-eighths of the sulfur present in the pyritic form if added to the ash would restore the iron sulfide to the original form as weighed.

While with certain types of coal, especially those extensively used for steaming purposes, averaging 15 to 20 per cent ash, it is evident that there is a volatile ash constituent of considerable importance due to hydration of clayey material, in our present state of information as to the uniform distribution of this constituent it does not seem advisable to incorporate it in technical analyses. For a comparative study, however, a correction for this type of ingredient cannot be avoided. The factor which has received extended application is an increase of 8 per cent of the ash as weighed to represent this volatile constituent.

ALLOWABLE VARIATIONS

	Same analyst Per cent	Different analysts Per cent
No carbonates present.....	0.2	0.3
Carbonates present.....	0.3	0.5
Coals with more than 12 per cent ash..	0.5	1.0

SULFUR

By PERRY BARKER, *Chairman*

In view of the close agreement of results obtained in the experimental work on various types of coal, the Subcommittee recommends that a choice of the following three methods for the determination of sulfur be permissible:

- (a) The Eschka method.
- (b) The Atkinson method of fusion with sodium carbonate.
- (c) The method of fusion with sodium peroxide in the Parr calorimeter bomb.

I. THE ESCHKA METHOD

The essentials of this method as described by G. L. Heath¹ have been modified as given in the former report of the Committee of the American Chemical Society on Coal Analysis.² Additional directions for application when city gas is used are also included in the method herein recommended.

Thoroughly mix on glazed paper 1.3737 grams of coal and 6 grams of Eschka mixture. This mixture is prepared by thoroughly incorporating two parts of magnesium oxide with one part of sodium carbonate by passing through a 40-mesh screen. By this method of preparation the mixture attains a uniformity comparable with that of the laboratory sample of coal and thorough incorporation is, therefore, more easily effected. Transfer to a No. 1 Royal Berlin porcelain crucible and cover with about two grams of the Eschka mixture.

On account of the amount of sulfur contained in artificial gas, it is preferable to heat the crucible over an alcohol, gasoline or natural gas flame or in an electrically heated muffle. Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of sulfur. Heat the crucible slowly for about 30 minutes, gradually increasing the temperature and occasionally stirring until all black particles disappear, which is an indication of the completeness of the procedure.

The use of artificial gas for heating the coal and Eschka mixture is permissible, provided the crucibles are heated in a

muffle and a blank determination of the amount of sulfur absorbed from the gas is made.

Place the crucible in a cold gas muffle and gradually raise the temperature to about 870° or 925° C. (cherry-red heat) in about one hour. Maintain this maximum temperature for about one and a half hours and then allow the crucible to cool in the muffle. Remove and empty the contents into a 300 cc. beaker and digest with 200 cc. of hot water for one-half to three-quarters of an hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash five times, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 cc. with 10 to 20 cc. of saturated bromine water and make slightly acid with concentrated hydrochloric acid. Transfer the beakers to the hot plate and, upon boiling, precipitate the soluble sulfates by adding slowly from a pipet with constant stirring 10 cc. of a hot 10 per cent solution of barium chloride. Continue boiling for fifteen minutes and allow to stand for at least two hours at a temperature just below boiling. Filter through an ashless filter paper and wash first with hot water containing 1 cc. of hydrochloric acid per liter and then with hot distilled water until a silver nitrate solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of barium sulfate in a weighed platinum or alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. The paper should be smoked off gradually at first. After the paper is practically consumed raise the temperature to approximately 925° C. and heat to constant weight. In case artificial gas is used as a heating agent, a blank to correct for contamination due to sulfur in the gas is carried through the process in the manner described above, using the same amounts of Eschka mixture, wash water, bromine water, hydrochloric acid and barium chloride solution as employed in the regular determination. A large number of tests using a mixed coal and carburetted water gas containing not more than 25 grains of sulfur per 100 cubic feet show blanks averaging 0.003 gram of barium sulfate. These blanks include the impurities in the form of sulfur compounds in the reagents, which amount to nearly one-half of the total weights. The percentage of sulfur is obtained by deducting the blank, provided artificial gas is used, and multiplying the resulting figures by ten.

II. THE ATKINSON METHOD¹

Thoroughly mix on glazed paper 1.000 gram of the laboratory sample of coal with 7 grams of dry sodium carbonate and spread evenly over the bottom of a shallow platinum or porcelain dish. Place on a triangle slightly elevated above the bottom of a cold muffle. Raise the temperature of the muffle gradually until a temperature of 650° to 700° C. (dull red heat) has been obtained in half an hour and maintain this temperature for ten or fifteen minutes. The sodium carbonate should not sinter or fuse. The mixture should not be stirred during the heating process. When the dish has cooled sufficiently to handle, the matter should be examined for black particles of unburned carbon and in case such indications of incompleteness of the process appear, the dish should be replaced and heated for a short time. When all carbon is burned, remove the dish and digest the contents with 100 to 125 cc. of warm water. Allow the insoluble matter to settle, decant through a filter and wash several times by decantation. Transfer to the filter, adding a few drops of a solution of pure sodium chloride, if the insoluble matter tends to pass through the filter. The washing should be continued until the filtrate shows no alkaline reaction. Make the filtrate slightly acid with sufficient concentrated hydrochloric acid and precipitate the sulfates with barium chloride

¹ *J. Am. Chem. Soc.*, **20**, 630.

² *Ibid.*, **21**, 1127.

¹ *J. Soc. Chem. Ind.*, March 29, 1886. *J. Iron and Steel Inst.*, No. 2 (1896). *J. Am. Chem. Soc.*, **21**, 1128 (1899).

as described under the Eschka method. No oxidizing agent is required.

III. THE PEROXIDE FUSION METHOD

This method is most conveniently carried out in the bomb which is a part of the Parr calorimeter.¹ The sodium peroxide and potassium chlorate used in the fusion mixture should be of the grade especially prepared for the determination of heating values with this apparatus.

Before mixing the coal and chemicals for the fusion, thoroughly dry the bomb and warm slightly in order to be sure that all traces of moisture have been removed. Place one gram of potassium chlorate, about ten to twelve grams of specially prepared sodium peroxide and one-half gram of the laboratory sample of coal, which has previously been air-dried, in the bomb and seal quickly to avoid the absorption of moisture by the sodium peroxide. Shake the bomb thoroughly and rap sharply on the laboratory table to remove the portions of the mixture which may adhere to the top of the bomb on the terminals. Place in a vessel containing sufficient water to completely submerge the portion of the bomb containing the mixture, allowing the stem to protrude sufficiently to attach the terminals of the ignition circuit. Ignite the wire with a current of 15 to 20 volts either from a lighting circuit, four-cell storage battery or four or five dry cells in series. After the bomb has cooled, remove, dry, and open over a four-inch watch glass placed on top of the beaker in which the fusion is to be dissolved. The bottom of the bomb is removed and the fused mass is knocked out upon the watch glass with the special rod furnished with this apparatus. The portions of the fusion which adhere to the sides and top of the bomb are washed into the beaker with hot water, the remainder of the fused mass is added and completely dissolved. The solution is acidified with hydrochloric acid in such a manner as to give approximately 5 cc. of free acid in the entire volume, which should amount to 250 to 300 cc. of liquid. Heat the solution, filter through a qualitative filter and wash several times with hot water. Heat the filtrate to boiling and precipitate the soluble sulfates by slowly adding 10 cc. of the hot solution of barium chloride. Continue the boiling for fifteen minutes and allow to stand for at least two hours at a temperature just below boiling. Filter, wash and ignite as described under the Eschka method. Particular care should be taken in washing the precipitate obtained by this method in order to remove all of the soluble salts which are formed in the fusion process.

Experimental Results.—The above recommendations have been made after careful consideration of all the available methods for the determination of sulfur in coal. In order to make careful tests of such methods, a number of samples were prepared which represented various types of coal having sulfur contents ranging from one to four per cent. The results of comparative tests for the various methods are given in Table I. This same set of samples was submitted to two other members of the committee for comparative tests. One member employed the Eschka method essentially as given in this report while the other followed the Peroxide Fusion method. The results of these determinations, together with the original figures from Table I for the various methods are given in Table II.

In connection with the report on the various methods for the determination of sulfur in coal, the results of comparative tests by a member of the committee² are of particular interest. The results of these tests on 35 samples³ of coal show an average difference of 0.02 per cent of sulfur between the Peroxide Fusion method and the Eschka method on the samples which averaged slightly over two per cent of sulfur. The average results from the bomb washings were 0.16 per cent lower than by the Per-

oxide Fusion method, while the results by the special Photometric method were 0.11 per cent. lower than by the Peroxide Fusion method.

After careful consideration of the various methods, together with the data which are given herewith, the Subcommittee recommends that the method of precipitation from bomb washings be discarded and endorse a choice between the (1) Eschka method, (2) the Atkinson method and (3) the method of fusion with sodium peroxide in the Parr calorimeter.¹

TABLE I COMPARATIVE TESTS
Determination of Sulfur in Coal by Various Methods
Percentages Refer to Dry Coal Basis

SAMPLE	I	II	III	IV	V	VI	VII	
							(a)	(b)
1.....	1.02	0.000	1.01	1.00	1.03	1.06	1.01	1.02
2.....	1.99	0.017	2.00	2.02	1.94	2.01	1.79	1.92
3.....	2.98	0.004	3.02	2.99	2.93	3.04	3.00	3.13
4.....	3.95	0.019	3.97	3.96	3.87	3.94	3.91	3.94
(Dup.).....	3.96							

I. Eschka method: Samples heated in gas-fired muffle, corrected for blank determination due to sulfur in gas, which averaged 0.025 per cent. This process is regularly in use in the laboratory where these tests were made.

II. Residual sulfur on extracting residue from Eschka method with hydrochloric acid.

III. Eschka method, according to methods for coal analyses adopted by the American Chemical Society in 1899, using the alcohol lamp.

IV. Atkinson's fusion method: "Method of Fusion with Sodium Carbonate," *J. Am. Chem. Soc.*, **21**, 1128.

V. Precipitation from washings obtained by combustion in oxygen bomb calorimeter.

VI. "Parr's Method of Combustion and Fusion in Bomb with Sodium Peroxide," *THIS JOURNAL*, **1**, 689 (1909).

VII. "Precipitation of Soluble Sulfates from Washings Resulting from Combustion of Coal in Oxygen Bomb Calorimeter by means of Barium Hydrate and Subsequent Neutralization and Titration with Standard Alkali and Acid," *Z. chem. Apparatenkunde*, **2**, 542; (a) and (b) are duplicate determinations on same sample.

TABLE II
Determination of Sulfur in Coal (Results on Standard Samples)
Percentages Refer to Dry Coal Basis

SAMPLE	Eschka method		Peroxide fusion method	
	Table I	Analyst A	Table I	Analyst B
1.....	1.02	1.03	1.06	1.02
2.....	1.99	1.98	2.01	2.01
3.....	2.98	2.92	3.04	3.01
4.....	3.95	3.86	3.94	4.03

ALLOWABLE VARIATIONS

	Same analyst Per cent	Different analysts Per cent
For coal.....	0.05	0.1
For coke.....	0.03	0.05

DETERMINATION OF THE CALORIFIC POWER

By H. C. DICKINSON, Chairman

The specifications are to be of two classes, (a) and (b). The procedure specified under (a) may be followed in tests where a tolerance of at least 1 per cent is allowed. The procedure under (b) is to be used in all cases where the limit of tolerance is less than 1 per cent, and is to be followed in all cases of dispute. Under (b) any three determinations made at the same time on the same sample may be required to fall within a range of 0.3 per cent.

Combustion Bombs.—The Atwater, Emerson, Mahler, Peters, Williams or similar bombs may be used. For (a) the lining material of the bomb need not be specified. The Parr calorimeter may also be used, but only on condition that both parties to the contract agree to its use. For (b) the bomb shall have a lining of platinum, gold, porcelain enamel or other material

¹ A simpler, inexpensive bomb is described in *Am. Chem. J.*, **25**, 184 (1903); see also Noyes, "Organic Chemistry for the Laboratory," p. 21.

² *THIS JOURNAL*, **1**, 689 (1909).

³ Mr. Fieldner recommends that precipitation from the bomb washings be permitted when both parties agree to its use, especially for coals used for steaming or heating purposes.

which is not attacked by nitric and sulfuric acids, or other products of combustion.

Calorimeter Jacket.—The calorimeter (except the Parr) must be provided with a water jacket, having a cover to protect the calorimeter from air currents. The jacket must be kept filled with water. For (b) the water in the jacket must be kept within 2 or 3 degrees of the temperature of the room and should be stirred continuously by some mechanical stirring device.

Stirring of the Calorimeter Water.—The water in the calorimeter must be stirred sufficiently well to give consistent thermometer readings while the temperature is rising rapidly. The speed of stirring should be kept constant. For (b) a motor-driven screw or turbine stirrer is recommended and the speed should not be sufficient to hold the temperature of the calorimeter more than 0.3° or 0.4° C. above that of the jacket, when the stirrer is allowed to run continuously. Accurate results cannot be obtained when too much energy is supplied by the stirring device or when the rate of stirring is too irregular. The portion of the stirring device immersed in the calorimeter should be separated from that outside by nonconducting material, such as hard rubber, to prevent conduction of heat from the motor or outside air.

Thermometers.—Thermometers used shall have been certified by a government testing bureau and shall be used with the corrections given on the certificate. This shall also apply to electrical resistance or thermoelectric thermometers. For (b) correction shall also be made for the temperature of the emergent stem of all mercurial thermometers, and for the "setting" of Beckmann thermometers. For accurate work either Beckmann or special calorimetric thermometers graduated to 0.01° or 0.02° are required. Such thermometers should be tapped lightly just before each reading to avoid errors due to the sticking of the mercury meniscus, particularly when the temperature is falling. A convenient method is to mount a small electric buzzer directly on the top of the thermometer and connect it up with a dry cell and a push button. The button should be pressed for a few seconds immediately before each reading.

Oxygen.—Oxygen used for combustions shall be free from combustible material and for (b) it shall not contain more than 5 per cent nitrogen and argon together. The total amount of oxygen contained in the bomb for a combustion shall not be less than 5 grams per gram of coal. But the combustion must be complete as shown by the absence of any sooty deposit on opening the bomb after firing.

Firing Wire.—The coal in the bomb may be ignited by means of either iron or platinum wire. If iron wire is used, it should be of about No. 34 B. & S. gauge and not more than 10 cm. (preferably 5 cm.) should be used at a time. A correction of 1600 calories per gram weight of iron wire burned is to be subtracted from the observed number of calories. Except, however, that this correction may be omitted from both the standardizations of bomb and coal combustions, provided the same amount of wire is used in all cases.

Standardization.—The water equivalent of a calorimeter can best be determined by the use of standard substances such as the standard combustion samples supplied by the Bureau of Standards. The required water equivalent is equal to the weight of the sample multiplied by its heat of combustion per gram and divided by the corrected rise in temperature.

The calorimeter shall be standardized by the combustion of such standard samples supplied by the Bureau of Standards, and used according to the directions given in the certificates which accompany them. A standardization shall consist of a series of not less than five combustions of either the same, or different standard materials. The conditions as to amount of water, oxygen, firing wire, method of correcting for radiation, etc., under which these combustions are made shall be the same

as for coal combustions. For (b) in the case of any disagreement between contracting parties a check standardization shall be made at the time of test, but such standardization may consist of two or more combustions of standardizing samples.

Manipulation.—1. *Preparation of sample:* The ground sample, which is in approximate moisture equilibrium with the atmosphere, is to be thoroughly mixed in the bottle and an amount, approximately one gram, is to be taken out and weighed in the crucible in which it is to be burned. Coals which are likely to be blown out of the crucible should be briquetted. Standardizing samples are also to be briquetted. After weighing, the sample should preferably be immediately placed in the bomb and this closed. This procedure is necessary to avoid sublimation when naphthalene is used.

2. *Preparation of the Bomb.*—The firing wire, if iron, should be measured and coiled in a small spiral and connected between the platinum terminals, using, if necessary, a piece of platinum wire somewhat heavier than the iron wire, to make the connection. The platinum and the iron must both be clean. About 1/2 cc. of water should be placed in the bottom of the bomb to saturate, with moisture, the oxygen used for combustion. When the crucible is put in place in the bomb, the firing wire should touch the coal or briquet of standard material. For the combustion of standardizing samples iron wire is preferable to platinum.

3. *Filling the Bomb with Oxygen.*—Oxygen from the supply tank is to be admitted slowly to avoid blowing the coal from the crucible, and the pressure allowed to reach 20 atmospheres for the larger bombs or about 30 atmospheres for the smaller bombs, so that the bomb shall contain an amount of oxygen sufficient for complete combustion, viz., at least 5 grams per gram of coal, or other combustible. When feasible, the bomb may be exhausted before filling to remove the nitrogen of the air, thus reducing the amount of the nitric acid formed.

4. *Calorimeter Water.*—The calorimeter is to be filled with the required amount of water, depending upon the type of calorimeter. The amount may be determined either by measurement in a standardized flask or by weighing. For (b) distilled water should be used and the amount determined by weighing. The amount must be kept the same as that used in standardization of the apparatus, or a correction applied for the difference in weight.

5. *Temperature Adjustments.*—The initial temperature in the calorimeter should be so adjusted that the final temperature, after the combustion, will not be more than 1 degree, preferably about 1/2 degree, above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be very small when the rise of temperature is 2° or 3°, and the effect of evaporation will also be small.

6. *Firing Current.*—The electric current used for firing the charge should be obtained from storage, or dry cells having an E. M. F. of not more than 12 volts. The circuit should be closed by means of a switch which should remain closed for not more than two seconds. When possible, it is recommended that an ammeter be used in the firing circuit to indicate when the firing wire has burned out. For (b) the E. M. F. of the firing battery shall not exceed 12 volts, since a higher voltage is liable to cause an arc between the firing terminals, introducing additional heat, which cannot be measured with certainty.

7. *Method of Making an Observation.*—The bomb when ready for firing, is to be placed in the calorimeter, the firing wires connected, the cover put in place and the stirrer and thermometer so placed as not to be in contact with the bomb or container. The stirrer is then started and after the thermometer reading has become steady, not less than two minutes after the stirrer is started, temperatures are read at one-minute intervals for five minutes and the charge is then fired, noting the exact time of firing. Observations of temperature are then made at intervals de-

pending upon the method to be used for computing the cooling correction. When the temperature has reached its maximum and is falling uniformly, a series of thermometer readings is taken at one-minute intervals for five minutes to determine the cooling rate.

8. *Titration.*—After a combustion the bomb is to be opened, after allowing the gas to escape, and the inside examined for traces of unburned material or sooty deposit. If these are found the observations shall be discarded. If the combustion appears complete, the bomb is to be rinsed out and the washings titrated to determine the amount of acid formed. A correction of 230 calories per gram of nitric acid should be subtracted from the total heat observed. If the sulfur content of the coal is determined the amount of sulfuric acid should be computed and an *additional* correction of 1220 calories per gram of H_2SO_4 should be subtracted, for the excess of the heat of formation of the sulfuric acid over that of nitric acid.

Computation of Results.—The following method of computation is recommended, to take the place of the Pfundler or other similar formulas for computing the cooling correction (radiation correction).

Observe (1) the rate of rise (r_1) of the calorimeter temperature in degrees per minute for four or five minutes before firing, (2) the time (a) at which the last temperature reading is made immediately before firing, (3) the time (b) when the rise of temperature has reached six-tenths of its total amount (this point can generally be determined by adding to the temperature observed before firing, sixty per cent of the expected temperature rise, and noting the time when this point is reached), observe (4) the time (c) of a thermometer reading taken when the temperature change has become uniform some five minutes after firing, (5) the final rate of cooling (r_2) in degrees per minute for five minutes.

The rate r_1 is to be multiplied by the time $b - a$ in minutes and tenths of a minute, and this product added (subtracted if the temperature were *falling* at the time a) to the thermometer reading taken at the time a . The rate r_2 is to be multiplied by the time $c - b$ and this product added (subtracted if the temperature were *rising* at the time c and later) to the thermometer reading taken at time c . The difference of the two thermometer readings thus corrected, provided the corrections from the certificate have already been applied, gives the total rise of temperature due to the combustion. This multiplied by the water equivalent of the calorimeter gives the total amount of heat liberated. This result, corrected for the heats of formation of nitric and sulfuric acids observed and for the heat of combustion of the firing wire when that is included, is to be divided by the weight of the charge to find the heat of combustion in calories per gram. Calories per gram multiplied by 1.8 give the B.t.u. per lb. *See example.

The results should be reduced to calories per gram or B.t.u. per pound of *dry coal*, the moisture being determined upon a sample taken from the bottle at about the same time as the combustion sample is taken.

For an accurate comparison of different coals from the calorimeter determinations it is evident that the results should be reduced in each case by the heat of evaporation (preferably at 20° C.) of the water formed by combustion of the coal, since in the bomb this water is condensed and the heat of condensation is included in the measurement, while in nearly all commercial conditions the water vapor passes off uncondensed and the heat is lost. On account of the additional time required to determine the hydrogen content of coal samples the correction necessary to reduce to the above basis or "net" heat of combustion is not generally applied, although it may amount to several per cent in extreme cases.

Combustion of Anthracites and Coke.—For anthracites and

coke, which have a high ash content and do not readily burn completely, the following procedure is recommended:

The inside of the crucible is lined completely with ignited asbestos in a thin layer pressed well down into the angles. The coal is then sprinkled evenly over the surface of the asbestos. Otherwise the procedure is as previously described.

*EXAMPLE

Observations

Water equivalent 2550 g.

Weight of charge 1.0535

Approximate rise of temp. 3.2°

60 per cent of approximate rise 1.9°

Time Temp. Corrected temp.
10-21 15.244° (Thermometer corrections from the certificate)

22 .250

23 .255

24 .261

25 .266

(a) 26 .272

15.276°

Charge fired

(b) 27-12 17.201

¹ The initial temperature is 15.27°; 60 per cent of the expected rise is 1.9°. The reading to observe is then 17.2°.

(c) 31 18.500°

18.497°

32 .498

33 .497

34 .496

35 .494

36 .493

Computation

$r_1 = 0.028^\circ \div 5 = 0.0056^\circ$ per minute. $b - a = 1.2$ minutes

The corrected initial temperature

is $15.276^\circ + 0.0056^\circ \times 1.2 = 15.283^\circ$.

$r_2 = 0.007^\circ \div 5 = 0.0014^\circ$ per minute; $c - b = 3.8$ minutes

The corrected final temperature is $18.497^\circ + 0.0014 \times$

3.8..... = 18.502°

Total rise $18.502^\circ - 15.283^\circ$ = 3.219°

Total calories 2550×3.219 = 8209

Titration, etc..... = —7

Calories from 1.0535 grams coal..... 8202

Calories per gram..... 7785

or B.t.u. per lb..... 14013

In practice, the time $b - a$ will be found so nearly constant for a given calorimeter with the usual amounts of fuel that b need be determined only occasionally.

ALLOWABLE VARIATIONS

Per cent	Per cent
Same analyst..... 0.3	Different analysts..... 0.4

Parr Calorimeter.—The essential conditions for the operation of the Parr or peroxide calorimeter are as follows:

The coal should be finely pulverized. While 60 mesh is sufficient for bituminous coals, anthracites should be ground to at least 100 mesh.

The sodium peroxide used should be received in solder sealed tins and of a size suitable for emptying completely into the container for use, preferably a glass jar with lever sealed cap.

In addition to the reaction the peroxide serves as a diluent and the ratio necessary for a quiet reaction should be maintained, preferably 0.5 gram of coal to approximately 10 grams of peroxide. One gram of pulverized potassium chlorate is also used to advantage. It is first thoroughly mixed with the coal in such a manner as to avoid any possibility of lumping of these two substances. A thorough and uniform mixing with the peroxide is then assured by shaking in the closed cartridge.

Coals with moisture above 2 or 3 per cent must be oven-dried at 110° C. in the usual manner after weighing out, and before mixing with the chemicals.

The correction factors to be subtracted are as follows:

For each per cent. of ash.....	0.00278° C.
For each per cent. of sulfur.....	0.005° C.
For 1 gram of KClO ₃	0.130° C.
For electric fuse wire.....	0.008° C.
For oxygen of bituminous coals for 0.5 gram.....	0.025° C.
For oxygen of brown lignites for 0.5 gram.....	0.050° C.
For oxygen of benzoic acid for 0.5 gram.....	0.124° C.

The products of combustion, CO₂ and H₂O, combine with the chemical with the formation of heat, which amounts in each case to 27 per cent of the total heat of the reaction.

The corrections for ash, fuse wire, etc., in terms of the temperature rise together with radiation and thermometer corrections must first be subtracted from the indicated rise in temperature. The formula for the final calculation then becomes:

$$\text{Corrected thermometer rise} \times 0.73 \times \text{total water} = \text{calorific value.}$$

0.5 gram coal

Detailed directions for use of the calorimeter accompany each instrument and may be found in numerous handbooks such as the new edition of Hempel's "Gas Analysis," Olsen's "Quantitative Analysis," etc.

THE IRON AND STEEL INSTITUTE FELLOWSHIP

The Iron and Steel Institute of Great Britain have awarded the Carnegie Research Fellowship to Dr. Alcan Hirsch, of New York, for the purpose of carrying out investigations in connection with electric furnaces as applied to the heating of bars, billets and ingots.

This award carries a stipend of \$500.00.

The investigations will be carried out in Dr. Hirsch's laboratory in the Chemists' Building, New York City, and the results of his research will be presented before the Iron and Steel Institute at the annual meeting in May, 1914.

AMERICAN CHEMICAL SOCIETY—SEPTEMBER MEETING

The regular annual meeting of the American Chemical Society will be held in Rochester, New York, September 9th to 12th, inclusive. All members should keep these dates in mind and plan to be at the meeting.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

SIXTH SEMI-ANNUAL MEETING, BOSTON, JUNE 25-28, 1913

PROGRAM OF PAPERS

Meetings to be held at Engineers' Club.

Presidential Address. DR. T. B. WAGNER.

Effect of Climate on Plant Location. WM. M. BOOTH.

The Power Plant. MR. P. BARKER, of Arthur D. Little, Inc.

Relation of the Manufacturer to the Patent System. DR. WM. M. GROSVENOR.

General Efficiency in Dyehouses and Bleach Works. DR.

LOUIS J. MATOS.

Depreciation and Obsolescence. RICHARD K. MEAD.

Some Peculiar Functions of the Retained Expert. DR. WM.

M. GROSVENOR.

Legal Control of Dangers to Health in Factories. DR. CHAS.

E. MCKENNA.

Import Duties on Chemicals and their Influence on Chemical Industry. DR. F. W. FRERICHS.

The Drying of Linseed Oil and Red Lead with Special Reference to Painting Steel. DR. J. C. OLSEN AND A. H. CALLAGHAN.

EXCURSIONS

Hood Rubber Co., Watertown, Mass.

U. S. Arsenal, Watertown, Mass.

Laboratory and Experimental Paper Mill of A. D. Little, Inc., Boston.

Pacific Mills (Cotton Goods and Prints), Lawrence, Mass.

E. Frank Lewis' Wool Scouring Establishment, Lawrence

Russell Paper Co. (Wood Pulp by Soda and Sulfite Processes,

and Manufacture of Book and Print Paper), Lawrence

New England Gas and Coke Co., Everett, Mass.

New Power Plant of Boston Elevated Railroad.

Gorham Manufacturing Co. (Silversmiths and Goldsmiths, Plated Ware, Bronzes, etc.), Providence, R. I.

United States Finishing Co. (Large Cotton Finishing Plant.

Bleaching, Dyeing, Printing), Providence.

BUREAU OF STANDARDS' ANALYZED SAMPLES

The Bureau of Standards, Washington, D. C., has now ready for distribution samples of acid open hearth steel with 0.8 per cent and 1.0 per cent carbon, the fee being \$2.00 per bottle holding about 150 grams.

May 19, 1913

ANOTHER PLATINUM THIEF

On the night of May 16th, our laboratory was broken into and all of our platinum were stolen, presumably by a professional platinum thief. I have advised our company's plant managers and some other laboratories in this vicinity. The crook engineered the trick in a way somewhat similar to that used by the thief who was caught early this spring at Sparrows Point, Md. The man we suspect answers to the following description: about thirty-five years of age, very dark complexioned, smooth face, about five feet ten inches tall, weight about one hundred and forty pounds. He was neatly dressed, but not stylishly. He speaks fluent English, and one would probably take him to be either German or Jewish, but his accent would not reveal any particular race as far as I could detect.

L. SELMI, Chief Chemist

LAKE SUPERIOR IRON AND CHEMICAL CO.
ASHLAND, WIS.

BOOK REVIEWS

Chemical Industries of Belgium, Netherlands, Norway, and Sweden. By THOMAS H. NORTON. Bureau of Foreign and Domestic Commerce, Department of Commerce and Labor. Special Agents Series No. 65. Washington: Government Printing Office. 1912. 8vo. 85 pp. 21 tables.

It has been said that "the primary function of a consul is to extend the trade of the country which he represents..... It is his duty to be a close student of current events." The present report by Dr. Norton, who, through his extensive experience as a chemical works manager, teacher and original investigator, is familiar with the methods of scientific enquiry, deals in a most comprehensive manner, considering the extent of the field covered, with the supply of raw materials used in

the chemical industries, the methods of manufacture, the costs of production, and the foreign and domestic trade of each of the countries considered. Dr. Norton makes pertinent observations on the prospects of improving the chemical goods trade with the United States, and his accounts of the processes in operation in certain of the industries disclose many facts which will be new to some American manufacturers and teachers. The monograph makes extremely interesting reading, and demonstrates that the policy of detailing experts as special commercial agents is indeed a most commendable one.

The accounts of the Norwegian and Swedish industries, given by Dr. Norton, were published in full in *THIS JOURNAL*, 4, 51 and 691.

W. A. HAMOR

The Principles of Applied Electrochemistry. By A. J. ALLMAND, D.Sc. New York: Longmans Green & Co. 1912. 537 pp. Price, \$5.00 net.

This book is the first one in English which attempts to cover the field of applied electrochemistry and also the general theoretical considerations as well in one volume.

About one-third of the book is thus devoted to theory, which includes, for the most part, brief chapters on physical chemistry which are now to be found in many other books, but besides this there are many other subjects considered which are directly applicable to commercial processes, such as phenomena in molten electrolytes, the general principles of electrothermics, power, and electrical discharges through gases.

The remaining 300 pages deal with the subject of applied electrochemistry in detail, and the ground is covered for the most part in a very satisfactory manner. Space is saved to some extent by leaving out illustrations, indeed the various processes described are seldom illustrated at all and then usually by sketches.

The descriptions given of so large a number of processes are necessarily brief in many cases, but there is a large store of information exceedingly well presented which cannot fail to be of great value.

The subjects taken up in this special and technical part include primary and secondary cells, copper, silver, and gold.

Zinc, tin, nickel, iron and lead, electroplating and electrotyping, hypochlorites and chlorates, alkali and chlorine, and special electrochemical processes such as the production of hydrogen and oxygen.

Electrolysis in fused baths is considered under aluminium, sodium, calcium, magnesium, and zinc.

Electric furnace processes are described under steel refining, iron reduction, carbide and cyanamid, carborundum and graphite, alundum, carbon disulfide, and phosphorus.

The last two chapters deal with the oxidation of atmospheric nitrogen in the high tension arc and the production of ozone.

The subject matter is up-to-date as for example we find descriptions of the use of alternating currents in the Wohlwill process for gold refining, the Billette gravity cell for caustic and chlorine and the Fischer process for making ductile iron deposits of electrolytic iron.

The appendix has a table of current densities used in technical practice which runs from densities used in copper refining to the manufacture of carborundum; in the same way energy efficiencies per kilogram per K. W. hour, and ton yields per H. P. year are given.

As a whole the book is to be regarded as the best one that we have on this subject and one that will prove valuable to all concerned in this field of chemistry.

SAMUEL A. TUCKER

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York

Alkaloids, The Plant. By THOMAS A. HENRY. 8vo., pp. 466. Price, \$4.50. J. & A. Churchill, London.

Alumina, The Manufacture of. By A. BERGE. 8vo. Price, \$1.10. Wilhelm Knapp, Halle. (German.)

Ammonia, The Oxidation of, to Nitric and Nitrous Acid. By E. DONATH AND A. INDRÁ. Lex. 8vo., pp. 110. Price, \$1.25. F. Enke, Stuttgart. (German.)

Analysis, Methods of the "Verband der landwirtschaftlichen Versuchsstationen in Oesterreich." ANONYMOUS. 8vo., pp. 308. Price, \$2.00. Wilhelm Frick, Vienna. (German.)

Cement Specifications, A Treatise on. By J. COCHRAN. 8vo. Price, \$1.50. Constable & Co., London.

Chemical Engineering, The Elements of. By J. GROSSMANN. 2nd. Ed. Cr. 8vo., pp. 160. Price, \$1.00. C. Griffin & Co., London.

Chemical News, Collective Index, Vols. 1 to 100. ANONYMOUS. L. 8vo., pp. 712. Price, \$16.00. The Chemical News, London.

Coal, Sampling Deliveries, and Types of Government Specifications for the Purchase of Coal. By GEORGE S. POPE. 8vo., pp. 68. U. S. Bureau of Mines, Bulletin 63.

Colors, Oils and Varnishes, Manual of Painters'. By GEORGE H. HURST AND NOEL HEATON. 5th ed. 8vo. Price, \$2.75. Chas. Griffin & Co., London.

Dyeing, The Chemistry of. By JOHN K. WOOD. 8vo., pp. 80. Price, \$0.50. Gurney & Jackson, London.

Electrochemistry, Yearbook of. XIII. By HEINRICH DANNIEL AND JULIUS MEYER. Vol. 2. 8vo. Price, \$8.00. Wilhelm Knapp, Halle. (German.)

Explosives Used in Engineering and Mining Operations, Selection of. By CLARENCE HALL AND S. P. HOWELL. 8vo. pp. 50. U. S. Bureau of Mines, Bulletin 48.

Flour, Graham, Study of the Physical and Chemical Characteristics between Graham Flour and Imitation Graham Flours. By J. A. LECLERC AND B. R. JACOBS. 8vo. pp. 57. U. S. Dept. of Agriculture, Bureau of Chemistry, Bulletin 164.

Flue Gas, Apparatus for the Exact Analysis of. By GEO. A. BURRELL AND F. M. SEIBERT. 8vo. pp. 12. U. S. Bureau of Mines, Technical Paper 31.

Food Chemistry, Textbook of. By H. ROETTGER. 4th ed. 8vo. Price, \$4.00. Joh. Ambr. Barth, Leipzig. (German.)

Gas Producer in the United States, The Commercial Trend of the. By R. H. FERNALD. 8vo. pp. 92. U. S. Bureau of Mines, Bulletin 55.

Glycerin, its Production, Use and Determination. By S. W. KOPPE. 2nd Ed. 8vo. Price, \$0.75. A. Hartleben, Vienna. (German.)

Inorganic Chemistry, Handbook of the Methods of. Vol. 1. By ARTHUR STAHLER. 8vo. Price, \$7.00. Veit & Co., Leipzig. (German.)

Inorganic Chemistry, Technique of Experimental. By L. DOERNER. 4th ed. 8vo. pp. 1010. Price, \$6.50. Leopold Voss, Leipzig. (German.)

Iron, The Practical Use of the Testing of, by the Etching Process and by Aid of the Microscope. By E. PREUSS. 8vo. pp. 102. Price, \$1.00. Julius Springer, Berlin.

Iron and Steel. By O. F. HUDSON. 8vo. pp. 184. Price, \$1.50. Constable & Co., London.

Liquid Air, Oxygen, Nitrogen. By GEORGES CLAUDE. 8vo. 418. Price, \$1.50. J. & A. Churchill, London. (Translation.)

Natural Gas, Wastes in the Production and Utilization of, and Means for their Prevention. By RALPH ARNOLD AND F. G. CLAPP. 8vo. pp. 29. U. S. Bureau of Mines, Technical Paper 38.

Oil Industries, Chemistry of the. By J. E. SOUTHCORBE. 8vo. pp. 204. Price, \$2.00. Constable & Co., London.

Oils, Shales and Tars. (Translation.) By W. SHEITHAUER. 8vo. pp. 190. Price, \$2.25. Scott, Greenwood & Co., London.

Osmotic Pressure. By ALEXANDER FINDLAY. 8vo. pp. 84. Price, \$1.00. Longmans, Green & Co., New York.

Paper, Collective Index, Vols. 1 to 10. By THE EDITOR. quarto. pp. 9. Paper, Inc., New York.

Peat and Muck Deposits of Vermont. By J. L. HILLS AND F. M. HOLLISTER. 8vo. pp. 240. Vermont Agricultural Experiment Station, Bulletin 165.

Perfumery Manufacture, Modern. By H. MANN. 3rd ed. L. 8vo. Price, \$4.50. Verlag fuer Chemische Industrie, Augsburg. (German.)

Petroleum Products, The Preparation of Specifications for. By IRVING C. ALLEN. 8vo. pp. 12. U. S. Bureau of Mines, Technical Paper 36.

Power Engineering, Elements of Heat. By C. F. HIRSCHFELD AND W. N. BARNARD. 8vo. Price, \$5.25. Chapman & Hall, London.

Soaps. By RENE VALLIER. 8vo. pp. 156. Price, \$1.50. Gauthier Villars, Paris. (French.)

Soaps, The Modern Manufacture of Toilet. By J. SCHALL. 8vo. Price, \$2.00. H. Ziolkowsky, Augsburg. (German.)

Sugar Manufacture. By SIEGMUND FEITLER. 8vo. Price, \$1.10. Alfred Holder, Vienna. (German.)

RECENT JOURNAL ARTICLES

Alcohol Rectification, New Methods of. By H. MASING. *Chemiker Zeitung*, Vol. 37, 1913, No. 33, pp. 329-330.

Alkali, Caustic, and Bleach. The Production of. By A. J. ALLMAND. *Chemical Engineering and The Works Chemist*, Vol. 3, 1913, No. 23, pp. 65-67.

Arsenic Used in Medicine, Synthetic Compounds of. By JAS. GIEBER. *Pharmaceutical Journal and Pharmacist*, Vol. 90, 1913, No. 2580, pp. 440-442.

Atmospheric Pollution, A Standard Method for the Investigation of. By JOHN B. C. KERSHAW. *Chemical World*, Vol. 2, 1913, No. 5, pp. 165-168.

- Boiler Troubles, their Causes, and their Prevention.** By ALBERT N. DUNHAM. *Industrial World*, Vol. 47, 1913, No. 18, pp. 532-534.
- Caustic Soda in Mercerizing, Reclaiming.** By RAFAELE SANSONE. *Textile World Record*, Vol. 48, 1913, No. 1, pp. 158-161.
- Cellulose, The Determination of Crude Fiber and.** By H. MATTHIES and F. HOERING. *Archiv der Pharmazie*, Vol. 251, 1913, No. 3, pp. 223-240.
- Cement, Contribution to the Study of.** By G. GIORGI and G. GALLO. *Pagella Chimica Italiana*, Vol. 53, Part I, 1913, No. 4, pp. 353-361.
- Chemistry, Applied, and Engineering, Recent Progress in.** By JAMES O. HANDE. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 1, pp. 1-62.
- Corrosion of Iron, An Electrolytic Theory of the.** By BERTRAM LAMBERT. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 5, pp. 272-274.
- Explosives, The Heat Test for.** By ALFRED C. EGERTON. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 7, pp. 331-341.
- Fats, The Analysis of, and the Chemistry of Fats, in 1912.** By W. EMERSON. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 27, pp. 181-197.
- Furnace, The Heat Balance of the Open Hearth.** By SIDNEY CORNELL. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 5, pp. 257-266.
- Gas Analysis, A Modification of the Jaeger Method of.** By S. H. WORRELL. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 5, pp. 245-257.
- Hydrocarbon and Carbon Chlorids.** By B. M. MARGOSCHES. *Chemiker Zeitung*, Vol. 37, 1913, Nos. 50 and 51, pp. 509-511, 519-520.
- Illuminating Gas Purification.** By A. S. B. LITTLE. *American Gas Light Journal*, Vol. 98, 1913, No. 18, pp. 282-287.
- Iron, Utility of Efficiency Records in the Manufacture of.** By J. J. PORTER. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 76, pp. 543-553.
- Lead Poisoning, Recent Progress in the Study of Industrial.** By C. A. KLEIN. *Chemical World*, Vol. 2, 1913, No. 5, pp. 153-156.
- Lubricants, The Use of Essential Oils, as.** By MAURICE PELLET. *Revista Industrial y Agrícola de Tucuman*, Vol. 3, 1913, No. 10-11, pp. 507-511.
- Metals, Electrical and Thermal Disintegration of.** By G. W. C. KAYE. *Chemical World*, Vol. 2, 1913, No. 5, pp. 149-153.
- Metals, The Hardness of.** By THOS. A. EASTICK. *Scientific American Supplement*, Vol. 75, 1913, No. 1948, pp. 277-278.
- Metals and Alloys, The Reaction of, with Nitric Acid.** By J. H. STANSBIE. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 7, pp. 311-319.
- Oil Engines for Textile Mills.** By FRANK CARTER. *Journal of the Textile Institute*, Vol. 3, 1912-13, No. 2, pp. 360-371.
- Oxidation, Studies on.** By H. E. ARMSTRONG and R. T. COLGATE. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 8, pp. 391-397.
- Oxy-cellulose.** By R. OERTEL. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 35, pp. 246-250.
- Paints, The Behavior of, under the Conditions of Practice, with Special Reference to the Aspersions Cast upon Lead Paint.** By HENRY E. ARMSTRONG and C. A. KLEIN. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 7, pp. 320-330.
- Paints, Comparison of Leadless, and Lead and Zinc.** By R. CLAUDE BUSSEL. *Oil and Colour Trades Journal*, Vol. 43, 1913, No. 757, pp. 1403-1408.
- Paper and Pulp under the Microscope.** By SINDALL and BACON. *Pulp and Paper Magazine of Canada*, Vol. 11, 1913, No. 8, pp. 254-255, to be continued.
- Petroleum, The Edeleanu Method for the Rectification of, by Means of Sulfur Dioxide.** By C. ENGLER and L. UBBELOHDE. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 27, pp. 177-181.
- Phosphorus, Determination of, in Iron and Steel.** By P. ARTMANN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1912, No. 29, pp. 203-208.
- Potash, Advances in the Industry, 1910-1912.** By HANS HOF. *Chemiker Zeitung*, Vol. 37, 1913, No. 40, pp. 401-404.
- Radioactivity.** By EDWIN P. ADAMS. *Proceedings American Institute of Electrical Engineers*, Vol. 32, 1913, No. 5, pp. 1159-1233.
- Rubber Varieties, The Commercial Nomenclature of Crude.** ANONYMOUS. *India Rubber World*, Vol. 48, 1913, No. 2, pp. 419-420.
- Rubber, Testing of Ebonite for Electrical Purposes.** By C. C. PATERSON, E. H. RAYNER and A. KINNES. *India Rubber Journal*, Vol. 45, 1913, No. 16, pp. 27-30.
- Sewage Purification in Color Factories.** ANONYMOUS. *Farber Zeitung*, Vol. 18, 1913, No. 26, pp. 1449-1452.
- Sewage and Sewage Effluents, Standards and Tests for.** By H. T. CALVERT. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 6, pp. 265-274.
- Silicates, Manufacture of Water Glass by the Fusion Method.** By HUGO KNOBLAUCH. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 35, pp. 250-254.
- Steel Works, The Technical Man and.** By W. E. SNYDER. *Proceedings Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 2, pp. 63-84.
- Sulfurous Acid, New Method for Titration of, as Well as of Sulfurous Acid in the Presence of Thiosulfuric Acid.** By E. ROSSARD and W. GROB. *Chemiker Zeitung*, Vol. 37, 1913, No. 46, pp. 468-469.
- Temperature Conversion Tables.** By LEONARD WALDO. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 76, pp. 558-559.
- Varnish and Color Industry in the Second Half of 1912, Progress in the.** By MANFRED RAGG. *Farben Zeitung*, Vol. 18, 1913, Nos. 27 and 28, pp. 1446-1447, 1497-1499.
- Wool, Desulphing of, before Scouring.** By J. F. WHITE. *Journal of the Textile Institute*, Vol. 3, 1912-13, No. 2, pp. 294-302.
- Zinc, The Electrometallurgy of.** By G. GALLO. *Gazzetta Chimica Italiana*, Vol. 43, Part I, 1913, No. 4, pp. 361-385.

PAPERS OF SPECIAL INTEREST TO INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS FROM THE SUPPLEMENTARY VOLUMES OF THE PROCEEDINGS OF THE EIGHTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.¹

- Alcohol, Methyl, New Method for the Identification of.** By P. N. RAIKAN. Vol. 25, pp. 417-19.
- Cellulose, Prolonged Action of Mixed Acid on.** By J. E. CRANE. Vol. 25, pp. 587-591.
- Coal Briquetting Industry, Commercial Aspects of.** By C. T. MALCOLMSON. Vol. 25, pp. 687-699.
- Corrosion, The Rate of Rusting of Iron and Steel.** By JAMES ASTON and CHARLES T. BURGESS. Vol. 26, pp. 453-469.
- Essential Oils, Contribution to the Unification of Methods of Analysis of.** By PAUL JEANCARD and CONRAD SATIE. Vol. 26, pp. 331-339.
- Essential Oils, Unification of Processes for Commercial Analysis and Valuation of.** By JOHN C. UMNEY and E. J. PARRY. Vol. 26, pp. 341-347.
- Explosives, Development in the U. S. during the Last Three Years.** By CHAS. E. MUNKOE. Vol. 25, pp. 245-254.
- Explosives, International Commission for Unification of the Testing Methods on the Stability of the.** By V. WATTEYNE. Vol. 25, pp. 255-304 and 305-314. (French and English.)
- Explosives, Methods for the Determination of the Effective Strength of High.** By ARTHUR M. COMEY and FLETCHER B. HOLMES. Vol. 25, pp. 217-233.
- Gas Analyses, Errors Resulting from Assumption that Molecular Volumes of All Gases are Alike.** By GEO. A. BURRELL and F. M. SEIBERT. Vol. 25, pp. 189-190.
- Iron Ores, Reduction of, in the Electric Furnace.** By D. A. LYON. Vol. 26, pp. 519-539.
- Natural Gas, Industrial Conditions of the Utilization of.** By C. T. MALCOLMSON. Vol. 25, pp. 701-709.
- Patents and Trade Marks.** By H. ISAY, et al. Vol. 26, pp. 653-694, 6 papers.
- Petroleum: New Methods in the Distillation of Oils with High Boiling Points.** By LEO STEINSCHNEIDER. Vol. 25, pp. 735-744. (German.)
- Petroleum, The Composition of the Mineral Oils with High Boiling Points.** By J. MARCUSON. Vol. 25, pp. 403-415. (German.)
- Phosphorus, Electric Heating and the Removal of, from Iron.** By A. E. GREENE. Vol. 25, pp. 191-200.
- Rubber, The Causes of the Natural Change in the Latex of Hevea Brasiliensis, and on the Depolymerization of Caoutchouc and its Conversion.** By G. STAFFORD WHITBY. Vol. 25, pp. 597-621.
- Steel, Electric Induction and Resistance Furnaces for.** By C. H. VON BAUR. Vol. 25, pp. 205-207.
- Tartaric Acid, The Determination of.** By P. B. DUNBAR. Vol. 26, pp. 361-373.
- Tartaric Acid, The Determination of Malic Acid and, in the Same Solution.** By P. B. DUNBAR. Vol. 26, pp. 375-386.
- Terpenes, Polymerization of Pinene.** By G. B. FRANKFORTER and F. W. POPPE. Vol. 25, pp. 363-370.
- Viscosity, Technical Applications of.** By ALBERT E. DUNSTAN and J. F. STREVEN. Vol. 25, pp. 647-660.
- Water, Report on Standardization of Methods on Determining, in Coals and Other Fuels and in Minerals.** By R. LESSING. Vol. 25, pp. 41-90.
- Water, What Hypochlorite Sterilization of, has Accomplished in Several Cities.** By C. A. JENNINGS. Vol. 26, pp. 215-239.
- Wood, Chemical Treatment of Waste.** By H. K. BENSON. Vol. 25, pp. 331-337.
- Wood Preserving Industry, The Development and Status of the, in the United States.** By E. A. STERLING. Vol. 26, pp. 17-30.
- Zinc, A Proposed Standard Method of Analysis for.** By FRANK G. BREYER. Vol. 25, pp. 7-37.

¹ For list of papers in the first twenty-four volumes, see THIS JOURNAL, 4, 779.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Separating Mixed Liquefied Gases. A. C. Morrison, March 18, 1913. U. S. Pat. 1,056,043. The process is designed for the production of gaseous oxygen and nitrogen from liquid air, and is based on the facts that oxygen is a paramagnetic element and that its magnetic susceptibility is higher than that of nitrogen.

The process consists in placing the liquid air or other mixture of liquefied gases within a strong magnetic field, and then allowing the liquid to become heated to a temperature slightly above the boiling point of the nitrogen, or other more volatile and less magnetic component, whereupon the nitrogen distills off, the oxygen, or other component, remaining by reason both of its relative involatility and of the tractive effect of the magnetic field.

Sulfite-Waste Explosive. F. Raschig, March 18, 1913. U. S. Pat. 1,056,366. This is a mixture of ammonium nitrate with dried sulfite waste constituents.

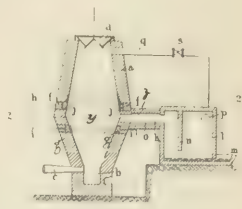
Refining Natural Gas Gasolene. W. O. Snelling, March 25, 1913. U. S. Pat. 1,056,845. By this continuous process, the liquid containing several volatile ingredients is heated in a series of condensers to a temperature sufficient to completely volatilize all of the ingredients, the vapors or gases being kept under

Gold Pigment. J. W. Hasburg, April 1, 1913. U. S. Pat. 1,057,422. A hydroxid, carbonate or bicarbonate of an alkali metal is added to a solution of gold chlorid and the gold precipitated by means of a metallic salt. The precipitate is washed and an acid added to dissolve the precipitated basic metal oxid from the gold.

Nitrate of Lime and Dicalcium Phosphate in a Single Operation. S. Peacock, April 1, 1913. U. S. Pat. 1,057,876. Finely divided phosphate rock containing tricalcium phosphate and lime is immersed in water and gases containing nitric acid blown through the mixture until the free lime and one-third of the combined calcium in the tricalcium phosphate are converted into calcium nitrate. The resulting calcium nitrate and dicalcium phosphate are suitable for plant food.

Production of Zinc and the Like. A. B. Pescatore, Apr. 1, 1913. U. S. Pat. 1,057,878.

Zinc ore and a reducing body are fed into a shaft or like blast furnace and a slow current of air supplied in such quantity as to reduce the ore but without permitting the oxygen to reach the reducing zone. The reduction zone is maintained at high temperature by electric heating.



New Form of Synthetic Indigo. A. Schmidt and A. Steindorff, April 1, 1913. U. S. Patent 1,057,886. Indol derivatives, preferably leuco-indigo salts, are subjected to oxidation in the presence of a phenol.

Treatment of Copper Ores Bearing Precious Metals. J. C. Clancy, April 1, 1913. U. S. Patent 1,057,936. The ores are subjected to the action of a cyanid solution containing a soluble cyanamid and the solution electrolyzed for the recovery of the copper.

Process of Making Caoutchouc Substances. C. Harries, April 8, 1913. U. S. Patent 1,058,056. The patentee has discovered that the alkali and alkaline earth metals are capable of converting hydrocarbons of the butadiene series, such as butadiene and its homologous and substitution products, into new caoutchouc substances. In the process 5 parts of sodium wire are pressed into 1000 parts of butadiene. The container is closed and allowed to stand for a week or two. The sodium is then acted upon by alcohol or water and the caoutchouc substance formed rolled into sheets. The product is an elastic whitish substance soluble in benzene.

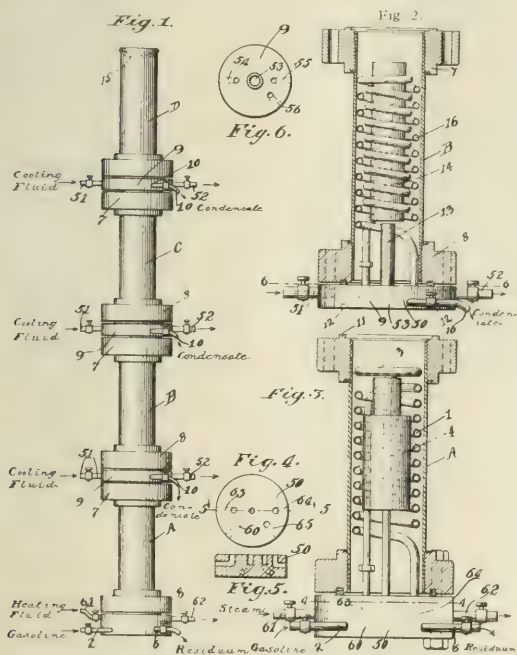
Baking Powder. E. Jacoby, April 15, 1913. U. S. Patent 1,058,980. The composition contains an oxygen-yielding per carbonate.

Malleable Iron Direct from Ore. A. R. Lindblad. April 15, 1913. U. S. Patent 1,058,991. A shaft furnace is charged with a mixture of the ore and reducing material. Gases taken from the shaft are heated outside the furnace and introduced into the shaft to reduce the ore. The resulting mass is then passed without cooling or contact with air into an electric melting furnace.

Low-Carbon Nickel Alloys. E. A. Byrnes, April 22, 1913. U. S. Patent 1,059,709. High-carbon ferrochromium is reacted upon with nickel oxid by feeding the nickel oxid into a bath of calcium aluminate slag supported on the molten ferrochromium.

pressure in excess of two atmospheres. This pressure is so high that the boiling points of the several ingredients are widely separated: each ingredient or fraction containing several ingredients is thus separately condensed, at a temperature slightly below its boiling point.

Concentrating Sulfite Waste Liquor. C. Ellis, April 1, 1913. U. S. Pat. 1,057,416. Air is blown through the sulfite liquor to remove a portion of the free sulfurous acid. The residue is neutralized to alkaline reaction, concentrated under reduced atmospheric pressure and freed from insoluble products by hydrolysis.



MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF MAY, 1913

ORGANIC CHEMICALS

Acetanilid.....	Lb.	21 @	23
Acetic Acid (28 per cent).....	C.	2 00 @	2 15
Acetone (drums).....	Lb.	16 1/2 @	17 1/2
Alcohol, denatured (180 proof).....	Gal.	37 @	39
Alcohol, grain (188 proof).....	Gal.	2 50 @	2 55
Alcohol, wood (95 per cent).....	Gal.	49 @	52
Amyl Acetate.....	Gal.	2 35 @	2 55
Aniline Oil.....	Lb.	10 1/8 @	10 5/8
Benzoic Acid.....	Lb.	23 @	27
Benzol (90 per cent).....	Gal.	21 @	23
Camphor (refined in bulk).....	Lb.	42 1/2 @	44
Carbolic Acid (drums).....	Lb.	12 @	14 1/2
Carbon Bisulfide.....	Lb.	6 1/2 @	8
Carbon Tetrachloride (drums).....	Lb.	8 @	8 1/2
Chloroform.....	Lb.	25 @	35
Citric Acid (domestic), crystals.....	Lb.	41 1/2 @	42 1/2
Dextrine (corn).....	C.	2 80 @	3 40
Dextrine (imported potato).....	Lb.	6 @	7
Ether (U. S. P., 1900).....	Lb.	14 @	20
Formaldehyde.....	Lb.	8 1/2 @	9 1/2
Glycerine (dynamite).....	Lb.	19 @	19 1/2
Oxalic Acid.....	Lb.	8 @	8 1/4
Pyrogallie Acid (bulk).....	Lb.	1 20 @	1 40
Salicylic Acid.....	Lb.	29 @	31
Starch (cassava).....	Lb.	3 1/4 @	4
Starch (corn).....	C.	2 02 /	2 50
Starch (potato).....	Lb.	4 1/4 @	5
Starch (rice).....	Lb.	8 @	9
Starch (sago).....	Lb.	29 @	29 1/4
Starch (wheat).....	Lb.	5 @	6
Tannic Acid (commercial).....	Lb.	35 @	35 1/2
Tartaric Acid, crystals.....	Lb.	30 1/4 @	31

INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 3/4 @	8
Acetate of Lime (gray).....	C.	2 50 @	2 60
Alum (lump).....	C.	1 75 @	2 00
Aluminum Sulfate.....	C.	1 40 @	1 75
Ammonium Carbonate, domestic.....	Lb.	8 @	8 1/2
Ammonium Chloride, gray.....	Lb.	6 1/4 @	6 1/2
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4 @	2 1/2
Arsenic, white.....	Lb.	4 @	4 1/2
Barium Chloride.....	C.	1 70 @	1 80
Barium Nitrate.....	Lb.	5 1/4 @	5 1/2
Barytes (prime white, foreign).....	Ton	18 50 @	22 50
Bleaching Powder (35 per cent).....	C.	1 25 @	1 40
Blue Vitriol.....	Lb.	5 1/4 @	5 1/2
Borax, crystals (bags).....	Lb.	39 1/4 @	41 1/4
Boric Acid, crystals (powd.).....	Lb.	7 @	7 1/2
Brimstone (crude, domestic).....	Ton	22 00 @	22 50
Bromine, bulk.....	Lb.	30 @	35
Calcium Chloride, fused.....	C.	85 @	1 10
Chalk (light precipitated).....	Lb.	4 @	5
China Clay (imported).....	Ton	11 50 @	18 00
Feldspar.....	Ton	7 00 @	9 00
Fuller's Earth, powdered, Foreign.....	Ton	14 50 @	15 00
Green Vitriol (bulk).....	C.	55 @	60
Hydrochloric Acid (18°).....	C.	1 15 @	1 55
Iodine (resublimed).....	Lb.	3 05 @	3 10
Lead Nitrate.....	Lb.	8 1/2 @	8 1/4
Litharge (American).....	Lb.	6 1/2 @	7
Lithium Carbonate.....	Lb.	65 @	70
Magnesia (powdered).....	Lb.	5 1/2 @	6
Magnesite (raw).....	Ton	30 00 @	31 00
Nitric Acid, 36°.....	Lb.	37 1/8 @	41 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	21 1/2 @	25 1/2
Phosphorus.....	Lb.	35 @	40
Plaster of Paris.....	Bbl.	1 50 @	1 70
Potassium Bichromate, 50°.....	Lb.	6 3/4 @	7
Potassium Bromide.....	Lb.	39 @	40
Potassium Carbonate (calcined) 80 @ 85%.....	C.	3 40 @	3 65
Potassium Chlorate, crystals.....	Lb.	8 1 @	9 1
Potassium Cyanide (bulk) 98-99%.....	Lb.	19 @	24
Potassium Hydroxide.....	C.	3 75 @	4 75
Potassium Iodide (bulk).....	Lb.	2 60 @	2 65
Potassium Nitrate (crude).....	Lb.	5 @	—
Potassium Permanganate (bulk).....	Lb.	98 1/4 @	11
Quicksilver, Flask.....	40 00 @	—	—
Red Lead (American).....	Lb.	6 1/2 @	7
Salt Cake (glass-makers').....	C.	55 @	65

Silver Nitrate.....	Oz.	38 3/4 @	40
Soapstone in bags.....	Ton	10 00 @	12 00
Soda Ash (48 per cent).....	C.	65 @	70
Sodium Acetate.....	Lb.	4 @	4 1/2
Sodium Bicarbonate (domestic).....	Lb.	1 @	1 1/4
Sodium Bicarbonate (English).....	Lb.	2 1/4 @	3
Sodium Bichromate.....	Lb.	4 1/2 @	4 1/4
Sodium Carbonate (dry).....	Lb.	60 @	80
Sodium Chlorate.....	Lb.	8 1/4 @	9 1/2
Sodium Hydroxide, 60 per cent.....	C.	1 57 1/2 @	1 62 1/2
Sodium Hyposulfite.....	C.	1 30 @	1 60
Sodium Nitrate, 95 per cent, spot.....	C.	2 50 @	—
Sodium Silicate (liquid).....	C.	65 @	1 50
Strontium Nitrate.....	Lb.	6 7/8 @	7 3/8
Sulfur, Flowers (sublimed).....	C.	2 20 @	2 60
Sulfur, Roll.....	C.	1 85 @	2 15
Sulfuric Acid, 60° B.....	C.	85 @	1 00
Talc (American).....	Ton	15 00 @	20 00
Terra Alba (American), No. 1.....	C.	75 @	80
Tin Bichloride (50°).....	Lb.	14 1/4 @	14 1/2
Tin Oxide.....	Lb.	52 @	54
White Lead (American, dry).....	Lb.	5 1/4 @	6
Zinc Carbonate.....	Lb.	nominal	—
Zinc Chloride (granulated).....	Lb.	4 1/2 @	5
Zinc Oxide (American process).....	Lb.	5 3/8 @	6 3/8
Zinc Sulfate.....	Lb.	2 1/2 @	2 3/4

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	42 @	45
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2 @	14
Castor Oil (No. 3).....	Lb.	8 7/8 @	10
Ceresin (yellow).....	Lb.	12 @	22
Corn Oil.....	C.	5 60 @	5 65
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	44 1/2 @	45
Cottonseed Oil (p. s. y.).....	Lb.	7 10 @	—
Cylinder Oil (light, filtered).....	Gal.	21 1/2 @	32
Japan Wax.....	Lb.	9 1/4 @	10
Lard Oil (prime winter).....	Gal.	94 @	98
Linseed Oil (double-boiled).....	Gal.	49 @	50
Menhaden Oil (crude).....	Gal.	26 @	28
Neatsfoot Oil (20°).....	Gal.	98 @	1 10
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2 @	3 3/4
Paraffine Oil (high viscosity).....	Gal.	26 @	28
Rosin ("F" grade).....	Bbl.	5 15 @	5 25
Rosin Oil (first run).....	Gal.	34 @	38
Shellac, T. N.....	Lb.	18 @	19 1/2
Spermaceti (cake).....	Lb.	30 @	35
Sperm Oil (bleached winter), 38°.....	Gal.	72 @	74
Spindle Oil, No. 200.....	Gal.	18 @	19
Stearic Acid (double-pressed).....	Lb.	9 1/2 @	10
Tallow (acidless).....	Gal.	64 @	67
Tar Oil (distilled).....	Gal.	30 @	31
Turpentine (spirits of).....	Gal.	41 1/2 @	43

METALS

Aluminum (No. 1 ingots).....	Lb.	25 @	26
Antimony (Hallet's).....	Lb.	83 1/8 @	83 1/4
Bismuth (New York).....	Lb.	2 10 @	2 15
Bronze powder.....	Lb.	50 @	3 00
Copper (electrolytic).....	Lb.	15 55 @	15 3/4
Copper (lake).....	Lb.	15 70 @	15 7/8
Lead, N. Y.....	Lb.	4 35 @	4 40
Nickel.....	Lb.	50 @	55
Platinum (refined).....	Oz.	46 00 @	—
Silver.....	Oz.	60 7/8 @	61
Tin.....	Lb.	47 7/8 @	49
Zinc.....	Lb.	53 1/8 @	5 1/2

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	3 00 @	3 05
Blood, dried.....	Unit	2 90 @	2 95
Bone, 4 1/2 and 50, ground, raw.....	Ton	27 50 @	28 00
Calcium Nitrate (Norwegian).....	C.	2 40 @	—
Castor meal.....	Unit	2 80 &	10
Fish Scrap, domestic, dried.....	Unit	2 75 &	10
Mowrah meal.....	Ton	9 00 @	—
Phosphate, acid, 16 per cent bulk.....	Ton	7 50 @	8 00
Phosphate rock; f. o. b. mine:			
Florida land pebble, 68 per cent.....	Ton	3 00 @	3 25
Tennessee, 70-80 per cent.....	Ton	5 00 @	5 50
Potassium, "muriate," basis 80 per cent.....	Ton	38 55 @	—
Pyrites, furnace size, imported.....	Unit	0 13 1/2 @	—
Tankage, high-grade.....	Unit	2 90 &	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

JULY, 1913

No. 7

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhenny, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.
Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

No claims will be allowed unless made within 60 days

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:	Elfanite.....	606
The Index to Chemical Literature.....	The Industrial Uses of Calcium Carbide and Acetylene.....	606
534	The Employment of Liquefied Gases in Mining and Metallurgy.....	606
ORIGINAL PAPERS:	The Storage of Inflammable Liquids.....	607
Preliminary Report upon a Practical Accelerated Test for Paints and Varnishes. By A. M. Muckenfuss.....	Fuel Briquetting in the United States.....	607
535	"Parol".....	607
The Deterioration of Firebricks during Service. By Gilbert Rigg.....	Solid Alcohol.....	607
549	Benzole as a Motor Fuel.....	607
The Influence of Cinders on the Corrosion of Iron Imbedded in Clay. By Walter B. Schulte.....	A New Product from Whale Oil.....	608
554	The Composition of Some Sole Leathers.....	608
Recent Analyses of the Saratoga Mineral Waters. III. By Leslie Russell Milford.....	A New Horn Substitute.....	608
557	Some Industrial Uses of Sugar.....	608
The Precipitation of Gold by Manganous Salts. By A. D. Brokaw.....	Paints for Indicating the Uses of Pipes.....	609
560	A Self-Equalizing Expansion Joint.....	609
Soluble Arsenic in Mixtures of Lead Arsenate and Soap. By H. V. Tartar and L. A. Bundy.....	A New Type of Pulverizer.....	609
561	The Low Gas Producer and Engine.....	610
Mineralogical Soil Analysis. By Wm. J. McCaughey.....	A New Type of Recording Differential Pressure Gauge and Recording Flow-Rate Meter.....	610
562	The Status of the Ceresin Industry.....	610
On the Influence of the Lime-Magnesia Ratio. By P. L. Gile and C. N. Ageton.....	Horton Gas-Engine Packing.....	611
564	SCIENTIFIC SOCIETIES:	
A Simple Method for Preparing Neutral Ammonium Citrate Solution. By A. J. Patten and W. C. Marti.....	Prof. Dr. Paul Walden, President of the Ninth International Congress of Applied Chemistry. By George Frederick Kunz.....	611
567	A List of United States Public Documents Pertaining to Pulp and Paper.....	614
The Fluidity of Butter Fat and its Substitutes. By George F. White and Ralph H. Twining.....	American Chemical Society—New Descriptive Directory of the Division of Industrial Chemists and Chemical Engineers.....	616
568	OBITUARIES:	
The Properties of Watered Milk. By Edward W. Long and Clarence E. May.....	William McMurtrie.....	616
573	NOTES AND CORRESPONDENCE:	
The Determination of Nitrobenzol in Peanut Oil. By H. J. Lucas.....	The Sampling of Rubber Goods.....	618
576	Bakelite Patent Recognition.....	619
The Deterioration of Soda Water Due to Microorganisms. By N. P. Sherwood and C. C. Young.....	Note on the Standard Vanillin Solution for the Colorimetric Method for the Determination of Vanillin in Flavoring Extracts.....	619
577	Determination of Sulphate in Ammonium Sulfate Solutions, etc.—A Correction.....	619
LABORATORY AND PLANT:	The Chemical Constitution of Resinous Phenolic Condensation Products—A Correction.....	620
Some Projection Experiments with Spectra. By H. E. Howe.....	BOOK REVIEWS:	
578	A Dictionary of Applied Chemistry; Methods for the Analyses of Iron and Steel, Used in Laboratories of the American Rolling Mill Co., Middletown, Ohio; Coal, its Composition, Analysis, Utilization and Valuation; Electroplating; Food Inspection and Analysis.....	621
A Short Method to Determine the Efficiency of Oxides for Gas Purification. By A. F. Kunberger.....	NEW PUBLICATIONS.....	622
580	RECENT INVENTIONS.....	623
The Elimination of Rubber Stoppers from the Vitriified Clay Combustion Tube by Means of Tapered Clay Inlet and Outlet. By Chas. Morris Johnson.....	MARKET REPORT.....	624
581		
ADDRESSES:		
Expert Testimony—Its Materiality—Causes for Its Discredit—and Remedy. By Judge J. T. Ronald.....		
582		
The Smoke Nuisance; a Question of Conservation. By Raymond C. Benner and J. J. O'Connor, Jr.....		
587		
The Chemist and Scientific Management. By H. W. Gillett.....		
593		
The Interpretation of U. S. P. Assay Processes. By Frank O. Taylor.....		
601		
Water Supply for the Manufacturer. By W. M. Booth.....		
604		
CURRENT INDUSTRIAL NEWS:		
The Eynon-Evans Flanged Blow-off Valve.....		
605		
The Influence of Sulfur on the Stability of Iron Carbide in the Presence of Silicon.....		
605		
The Aluminum Industry.....		
606		

EDITORIALS

THE INDEX TO CHEMICAL LITERATURE

Under this title, the U. S. Patent Office has published a statement¹ describing the work undertaken by the Classification Division, so as to enable rapid and complete searches to be made on any subject of chemical literature. This is a gigantic piece of work, embracing not merely patent literature, but practically all fields of chemical literature.

Before the chemical card index was commenced, anything like a complete search of the literature was practically impossible, and the validity of chemical patents was more or less in doubt; for, after the most elaborate search possible was made, a five-line paragraph in the files of some little known chemical journal published in Japanese, Russian or other not readily understood language, would be sufficient if cited in court to invalidate the granted patent.

It will be several years before this card index is complete, although much assiduous work is being done on it. In the meantime, enough has already been accomplished that anyone making a search on the literature of a chemical subject, can save much labor and time by consulting the index of the Patent Office. It should be noted that the index is accessible not only to the examiners of the Patent Office, but to patent lawyers practising before the office, as well as to chemists and scientific workers all over the land. Hence, this card index is becoming a national monument to chemical literature.

For those not living too far away, a visit to Washington to consult the index may prove the shortest and cheapest way to make a search in chemical literature. It would be highly desirable, however, if duplicates of this index could be obtained for the more important libraries all over the country. It is true that copying this card index would be rather expensive, but there is no doubt that the enormous value of such a copy would be fully worth the expense. Why could not some of the libraries of the country work together and have several copies printed at the same time, and thus distribute the cost of the task among themselves?

It is interesting to quote from the report mentioned above:

"In planning the chemical card index, since it was manifestly impossible to index all chemical literature, it was decided to cover the work of the past by making a judicious selection of certain works of a general nature, such as the 20-volume work of Gmelin, the annual volumes of the Chemical Society of London, the 4-volume edition of Watts' "Dictionary of Chemistry," Richter's "Lexicon of Carbon Compounds," and other works of that character; by indexing these works the literature of the past would probably be as completely covered as it could be by any plan which the office had the force and means available for accomplishing."

"For the future it was proposed to keep the abstract journals

¹ Appendix K of the Report of the Investigation of the U. S. Patent Office, by the President's Commission on Economy and Efficiency, December, 1912. House of Representatives, 62d Congress, 3d Session, Document No. 1110.

of the Chemical Society of London, the German abstract periodicals, *Berichte* and the *Centralblatt*, and other works of that character indexed up to date."

"Later when the American Chemical Society, in 1907, commenced the publication of its very complete set of abstracts, it was determined to omit the periodicals in German and other foreign tongues, and retain in the card index only the yearly index volume of the Chemical Society of London in addition to the American abstracts."

The above reference to the usefulness of the abstracts of the American Chemical Society would be decidedly more satisfactory if it were not accompanied by the following statement:

"The question has been raised whether the annual index of the Chemical Society of London is not duplicated by the work of the American abstractors to such an extent as to render it useless to include both publications in the index."

"It is found upon comparing the published lists of the publications indexed by each set of abstracts as follows:

Publications abstracted by the London Society.....	101
Publications abstracted by the American Society.....	516
Publications abstracted by the London Society not abstracted by the American....	29

These 29 publications not covered by our American workers include the following *viz.*: German, 8; English, 12; Dutch, Swedish, and French, 2 each; and 1 each of Italian and Japanese.

"Comparing 6 pages of the English Society Index of 1909 with the corresponding American work of the same year it is found that out of 256 articles and monographs indexed by the English workers, 159 of these articles were not in any way referred to in the American Society Abstracts."

"These two facts together seem to fully answer the question, and show the necessity of including both works in the index."

May this criticism stimulate our American abstractors to greater zeal and accuracy, aside from the fact that many justified criticisms have been made that in some instances the abstracts are carelessly drawn up and give a very wrong idea of the originals.

Various difficulties were encountered in outlining a general plan for the index. If chemical bodies each had but one instead of several names, and if in chemical literature one never met with bodies as yet unnamed and therefore referred to by chemical formulas only, then undoubtedly the dictionary plan pure and simple, with the names of the substances alphabetically arranged and the references to literature and patents collected under their proper titles, would answer every requirement, and would be, in fact, the only proper system to use. Practically, however, most bodies known to chemists have a plurality of names, and the names approved and used in prior decades are generally not the names in highest repute nor in ordinary use to-day, nor is it at all sure that the names now in use will in most or even in many cases remain in use in years to come.

Where a chemical compound has several names (as indeed is usually the case), were it possible to decid

now (which perhaps might be done) which one of them is, on good scientific grounds, the most appropriate for index purposes in view of present knowledge, and further (which of course could not be done), could one be assured that such name would remain the approved name for all future time, such title could, without hesitation, be now adopted as the indexing title, under which all references to literature or patents could be entered, and all other titles and names cross-referenced into it; but while this might be done now in certain cases, which and how many of these names now used and approved will remain in use in years to come is something that no one can at present determine. Evidently the dictionary plan, unmodified, was not the best, and some better system had to be devised not open to these objections.

The system adopted was based on the chemical formula. In establishing for the Patent Office a card index to chemical literature, it was therefore decided to use, as an indexing basis, the kind and number of the component atoms of a chemical compound, these being its most unvarying characteristics, being subject only to errors of chemical analysis, and being, therefore, the most stable and unchanging basis for any scheme for the indexing and digesting of chemical literature: a conclusion reached at about the same time independently by Richter, as illustrated in his since published *Lexicon der Kohlenstoff-Verbindungen*, and by other later workers in this field, the Patent Office system differing from that of Richter in being simpler and of more general application.

It was found that the simplest, most certain, and most direct system, was to rewrite the so-called empirical chemical formula in a particular manner, that is to say, to write the atoms in the alphabetical order of their chemical symbols, upon library catalogue cards of standard size, and place these cards, arranged in alphabetical order, in standard library cases. For example, take the following chemical compounds:

$(\text{CH}_3)_2\text{C}_2\text{H}_2(\text{NO}_2)_2$	Dinitrobutane
$(\text{CH}_3)_2\text{CHNO}_2$	Isopropylic nitrite
$\text{KH}_2\text{C}_2\text{O}_4$	Potassium acetate
CH_3Cl	Methyl chloride
$\text{Cu}(\text{AsO}_3)_2$	Copper arsenite

Rewriting them and arranging them alphabetically by formulas instead of titles, they are:

As_2CuO_4	Copper arsenite
CH_3Cl	Methyl chloride
$\text{C}_2\text{H}_2\text{K}_2\text{O}_4$	Potassium acetate
$\text{C}_2\text{H}_7\text{NO}_2$	Isopropylic nitrite
$\text{C}_4\text{H}_8\text{N}_2\text{O}_4$	Dinitrobutane

It should be noted, however, that the compounds containing carbon and hydrogen, and broadly included in the domain of organic chemistry, constitute so large and important a class that it is fully justifiable to depart slightly from the strictly alphabetical arrangement of chemical symbols, and write C always first and H accompanying C always second, in order to bring more closely together in the index bodies more or less closely related in chemical and physical properties.

In practice, therefore, the following general rule has been followed in compiling the chemical card index of the Patent Office: Reject water of crystallization and rewrite the empirical formula in the alphabetical order of the chemical symbols, except that in carbon compounds, C is to be written first and H second. Follow this rewritten formula with the constitutional formula, when given, adding the water of crystallization, if any, but arrange the cards alphabetically by the rewritten formula.

The reason for disregarding water of crystallization may be illustrated as follows: The three bodies, Na_2SO_4 or anhydrous sodium sulfate, $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ or Glauber's salt, and the heptahydrated salt, $\text{Na}_2\text{SO}_4 + 7\text{H}_2\text{O}$, are in this way indexed under the same indexing formula, $\text{Na}_2\text{O}_4\text{S}$, and are thereby brought together, as they should be, for in solution they are chemically identical. If, on the other hand, water of crystallization were taken into account for indexing purposes, the corresponding indexing formulas would become $\text{Na}_2\text{O}_4\text{S}$, $\text{H}_{20}\text{Na}_2\text{O}_{14}\text{S}$, and $\text{H}_{14}\text{Na}_2\text{O}_{11}\text{S}$, respectively, and these three practically identical bodies would, in consequence, be widely separated in the index, which result would evidently be a very undesirable one.

The index was commenced and has been continued on the library-card catalogue plan, using the regular standard card, size $7\frac{1}{2}$ by $12\frac{1}{2}$ centimeters, or approximately 3 by 5 inches, without rulings except a single colored horizontal line $\frac{3}{8}$ of an inch below the top of the card—this for typewritten cards and cards upon which printed matter cut from books and periodicals is pasted. A limited use has also been made of cards having ruled lines, where for certain reasons the cards are written by hand.

I believe it would be very desirable to have an exchange of opinions on this subject in the correspondence column of this journal. It is our duty to assist by any helpful suggestions possible, the good work which is now being performed by the Washington Patent Office.

L. H. BAEKELAND

ORIGINAL PAPERS

PRELIMINARY REPORT UPON A PRACTICAL ACCELERATED TEST FOR PAINTS AND VARNISHES¹

By A. M. MUCKENFUSS

There being comparatively few constants in nature,

it follows that most materials are continually changing their properties with use, though at widely varying rates. In the case of paints, varnishes and some other materials affected by exposure to atmospheric agencies of destruction, this change of properties is quite rapid at first and continues generally at a di-

¹ Author's abstract of paper presented at the Milwaukee meeting of the American Chemical Society, March 25-28, 1913.

minishing speed. The coating when fresh is liquid, but soon becomes "tacky," and later firm but elastic, finally descending into a condition of brittleness, chalkiness, and other manifestations of old age. Among the properties of the paint and varnish film might be enumerated: permeability to various liquids and gases, electrical conductivity, elasticity, and hardness. All such characteristics are changing from the moment the coating is applied until it is finally destroyed. What is the internal cause of the alterations and to what extent are they independent of each other? It seems to be generally agreed that there are four classes of changes going on within a protective coating: A—*Chemical*: (1) Reactions between constituents of the air and the vehicle, gum, and in some cases the pigment. (2) Reactions between the coating and the surface covered. (3) Reactions upon each other of the various constituents of the coating. B—*Physical*: (4) Alterations in crystalline form, size of particles, and the like, in the pigment, and physical changes in the vehicle produced by the above chemical actions. The line of demarcation between the physical and the chemical is steadily growing more obscure and nowhere is its haziness more manifest than in such a complex mixture as that of the organic, inorganic, colloidal, crystalline materials of a paint film.

It being self-evident that reactions like the above are the causes of the aforesaid changes in properties, it seems to follow that, with the exception perhaps of the first physical alterations referred to, it is impossible for any one property of the film to gain or lose in value without also a difference becoming manifested in all the other properties. In other words, the variable properties of the paint and varnish coating are dependent and not independent functions. Here we have the foundation for the research outlined below. If the film becomes "flat," there will be an alteration of the density, permeability, hardness, and of all other properties. Theoretically, therefore, it is only necessary to measure one of these characteristics at various periods during the life of the coating in order to obtain an index of the alteration at all other points. Since the coefficient of change with time will be different for each property, the greater the number of these measured, the better; though from a practical view point, it may not be worth while to measure more than one accurately. These variables differ considerably in importance and ease of measurement. Some cannot be measured without injury to the film, as hardness, and some not without unfair treatment, as resistance to chemicals.

Of all these characteristics, permeability is second to none in importance and stands first in ease of measurement. It seems generally agreed among experts that differences in the permeability of the membranes lie at the base of the explanation of the wide contrasts between the durability of protective materials. Many methods, more or less accurate, have been devised for rating the perviousness of the paint film, in recognition of its importance as a distinct property, entirely aside from its periodic measurement as an

index to durability. As to the latter, the panel test is the standard and by its results, slowly obtained though they be, all other processes with similar purpose should be gauged. In the course of the numerous accelerated paint tests described in the literature, little attention has been paid to the age of film, thickness of coat, temperature and humidity of air, amount of sunshine, etc., after coats were applied. As will be shown later, no inferences can be drawn from measurements for the durability of membranes, unless all factors entering into the process of drying and decay are carefully standardized or unless all panels of a set of comparative tests are subjected to practically identical conditions as regards both intensity and duration.

The attempt was made at the outset of this investigation to devise for measuring permeability an apparatus that could be operated as accurately as needed, without in any way subjecting the membrane of the material to unfair treatment. Further

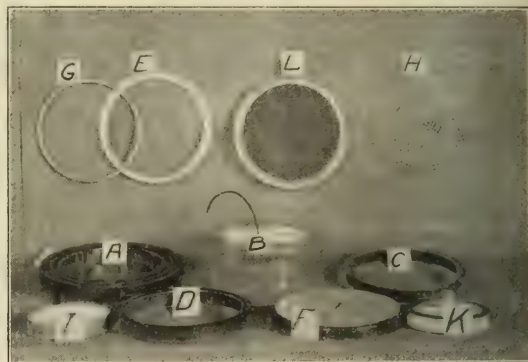


FIG. 1

objects were simplicity, ease of manipulation, a wide range of conditions for measurement, and the possibility of construction in various forms and from various materials. Fig. 1 exhibits several parts of the third and present form of the apparatus and Fig. 2 shows the parts assembled in several units arranged side by side on a shelf. In Fig. 1, A is the base; B, the general cover; D, the convex ring; C, the concave ring; E,



FIG. 2

the clamping ring; L, the two latter clamped together with a steel porous surface stretched tightly between them; F, the pan; G, the wire ring; H, the wire screen

disc; *K*, the weighed dish containing the water absorbent; and *I*, the corresponding unweighed dish. The cover to the weighed dish is sealed with a composite wax of proper viscosity. The materials used are cast iron, glass, and painted tin, but there is yet room for many improvements in this regard. When setting up this apparatus, the base is leveled and sufficient mercury is placed in each groove. Sufficient water is also poured into the central trough. Just beyond the water is a tube opening through a plug of cotton to the outside air and across from this is a similar space for placing another tube, if permeability to another gas besides water vapor is to be measured. The general cover of glass permits observation during the interval of a measurement and has a tube which serves both as a handle and as a means of communication with atmospheric pressure, the end of this tube being plugged with water absorbent and cotton to prevent ingress of moisture. The painted surface is prepared by first clamping or otherwise sealing the two rings together or the concave ring to the clamping ring by means of springs or wire through the small holes placed around at equal distances. A porous surface of strength and uniformity is placed between the rings before clamping and is automatically stretched because of the "dovetailing" of the parts into each other. This also minimizes danger of later leakage through points of contact. The porous surface is always of the same material that the paint is intended to cover, steel wire cloth for steel, hardened paper for wood, or cement and sand for concrete. This search for a satisfactory and fair imitation of the actual surface will continue to be the subject of study, commensurate with its importance.

The ring completed forms a "panel," the area of whose surface for painting is 341 sq. cm. The paint or varnish is applied uniformly with a brush just as to any other kind of panel or surface and by weighing before and after, the weight of coating may be obtained as accurately as desired, depending on whether the parts fit well and allow very little "dead" material to creep under the areas of clamping contact and whether or not the weighing is recorded immediately after each coat is spread.

The blank is run as follows: Invert the pan on the base and place on it the wire ring. Upon this place the wire screen disc and then the unweighed dish. Finally put the cover in position. After some hours, when a uniform condition has been reached, note the time, remove cover, replace the unweighed with the weighed dish, remove dish cover, and replace general cover. The next day, at the same time, raise general cover, replace cover of weighed dish and weigh the dish. The increase of weight in milligrams is the "blank" (generally about 50 milligrams) to be subtracted from the number of milligrams obtained in the next step. The pan is now removed and the panel whose permeability is sought is placed in position. After this, the steps are exactly as in the case of the blank. The final result gives the net milligrams for twenty-four hours. If the period is not twenty-four hours, the figure is calcu-

lated to that interval, which gives the "actual" permeability of the panel.

An inspection of the construction of the apparatus will demonstrate that, during the measurement, it is impossible for moisture to escape from the trough, except through the paint film of the panel. It is further impossible for it to enter or escape from the apparatus, disregarding any slight leakage, which is canceled by the blank. Both sides of the film are nevertheless open to atmospheric pressure; hence there is no excess in total pressure in any one direction. The area under the film has a humidity of 100 per cent, while that above has a humidity approaching as near to zero as the activity and quantity of the absorbent and the permeability of the film will permit. Under these conditions, the vapor is absorbed by the film on its under side and evolved on its upper side in a steady stream.

The mechanism by which the water or other substance passes through the film will be discussed in a later paragraph, when results bearing upon the point have been presented. Theoretically the standard value for permeability would be that obtained under standard conditions as regards each component that effects the result, or at standard temperature with unit area of film, unit weight or volume of coating, etc. At present, there is no need of attempting to establish such a standard. Practically, however, there is need of adopting a method of comparison by which successive results on the same and on different coatings may be compared with each other. The data to be presented later will indicate that, allowing for errors in spreading the paint already explained, the permeability decreases as the weight of the film increases. Whether the actual results times the weight of film equal a constant for the same coating will be determined by later measurements, but it seems to be true where the divergence in weight of film is not too large. The following proportion is then applicable: Weight of film in grams : 10 :: "weight permeability" : "actual permeability." In other words, the weight permeability represents the result that would be obtained if the film of area given had weighed exactly 10 grams. The major portion of the data presented in this paper is plotted on this basis, largely because the extra calculation involved slight additional labor and afforded the best ready means of comparison. It is true that a film weighing 5 grams would probably not have exactly twice the permeability of one of the same material weighing the standard 10 grams but if 5 grams is the weight of the regulation number of coats for that material, the results on 5 grams should be the basis of calculation. If the densities of the liquids are very divergent some other means of comparison must be adopted before it can be stated that one substance is "high" and another "low" in perviousness. While the "actual" permeability makes comparison on the basis of equal number of coats, yet a "coat" may vary greatly according to the thickness and spreading qualities of the material applied. Of course both the weight and volume of a coating change with time,

but it would appear unnecessary to make more than one determination of these under uniform conditions in order to secure a comparison sufficient for all practical purposes.

One of the first points noticed during this investigation was that successive measurements on the

were reversed, and finally the panel brought to its original position. Thus the moisture passed first from the inside out, and this direction was reversed twice for the white and once for the varnish. This order was changed in the case of corroded lead, with also two reversals.

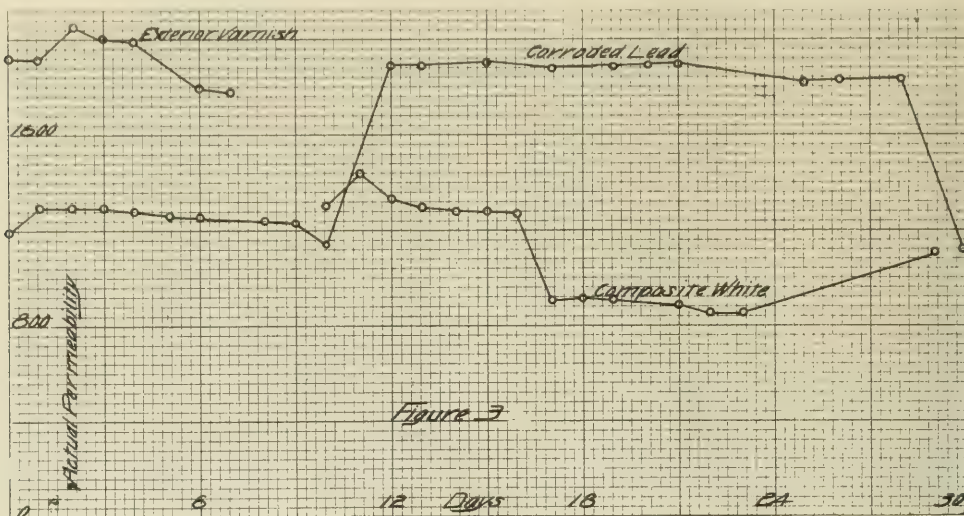


Figure 3

same panels without intervening exposure did not check with each other. This was not surprising since an appreciable temperature coefficient was to be expected. Unless otherwise stated, the results presented in this paper were under conditions of sufficiently uniform temperature, on the average 32.9°C . The exact coefficient under all conditions will be a matter for later determination. The effect of temperature is marked. Thus, it was found that the panel of white (Fig. 3) which gave a permeability of 854 and 853, successively, at 32.9°C ., gave two days later, with no intervening exposure, 137 and 139 at 10.9°C ., or a drop of 32.52 milligrams for each degree. In this case, the coefficient is 0.0381 per degree C., based on the result at the higher temperature.

Measurements have been made on panels with no water in the trough underneath, with results of about 100 less the blank, representing the moisture actually in the film at the beginning. This is mentioned merely as proof that during the measurements the source of the water is ultimately in the trough of the base.

Fig. 3 is presented as a test of the accuracy of the apparatus under the degree of uniformity considered sufficient for practical purposes. Three panels were prepared at different times from concave and convex rings. Each was placed in a unit of the apparatus and kept there day after day with a dish of absorbent continually drawing water through the film. Generally it was a weighed dish and measurements were made daily, though this was not always convenient. For the varnish and composite white, the uncoated side was at first down; later the sides

RESULTS ON FIG. 3
CORRODED LEAD

Wt. of coat	Meas. No.	Days interval	Actual permeability	Meas. No.	Days interval	Actual permeability	Meas. No.	Days interval	Actual permeability
14.38	1	0	1197	2	1	1298	3	1	1296
	4	1	1292	5	1	1273	6	1	1251
	7	1	1253	8	2	1241	9	1	1223
	10	1	1156	11	2	1894	12	1	1889
	13	2	1896	14	2	1839	15	2	1847
	16	1	1869	17	1	1868	18	4	1812
	19	1	1821	20	2	1830	21	2	1110

OUTSIDE WHITE

1	0	1302	2	1	1445	3	1	1339
4	1	1298	5	1	1285	6	1	1285
7	1	1261	8	1	910	9	1	918
10	1	903	11	2	884	12	1	854
13	1	853	14	6	1106

EXTERIOR VARNISH

1	0	1915	2	1	1911	3	1	2049
4	1	2001	5	1	1995	6	2	1799
7	1	1775

It is easily apparent that the lead shows the greatest contrast and the exterior varnish the least, when comparing permeability on either side. Whether this expressed any particular advantage cannot yet be stated. The position of the panel on the base is important, but the length of time elapsing before a measurement is made after the panel is in position is unimportant for a small number of days. The steady decrease in permeability noticed is due doubtless to a slight drying action in progress even while the panel is on the base and in the absence of light. The fluctuations apparent enable one to gauge the degree of error probable for all other measurements to be submitted, which were made with the coated side up.

The most interesting point about Fig. 3 is the apparent fact, suspected by experts, that a paint film is more pervious in one direction than the other. Paint thus may have the advantage of "valve action," offering a greater resistance to water which tends to

same paint on the same surface will not last two years with a succession of bad seasons in a severe climate. In certain areas of the tropics situated on the southern slopes of mountains, we may actually see in nature practically all the extremes of temperature, light, and humidity regularly every twenty-four hours for

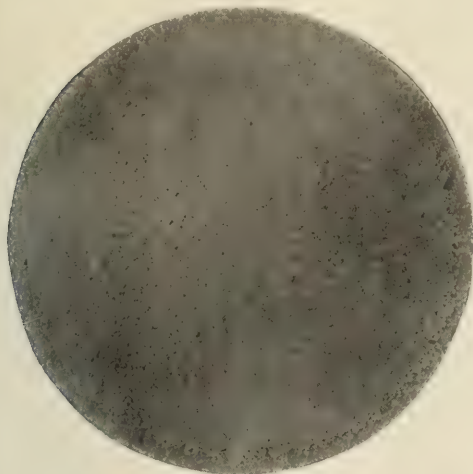


FIG. 4

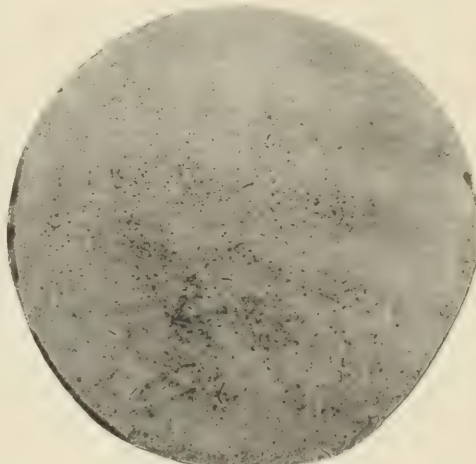


FIG. 5

reach the protected surface than to moisture which at other times and on wooden surfaces must be allowed to escape freely. This point will later receive further experimental trial, too many other phases of the research being more important at present. It may be concluded that the surface covered is probably the chief cause of the contrasts observed. A paint coating is in more intimate contact with the moisture of the under surface than with the moisture of the air (except during a rain). The under surface of wood during a measurement absorbs moisture more rapidly than the paint coating itself; hence, the permeability is higher from this direction.

PRACTICAL RESULTS ON PAINTS AND VARNISHES

It has been shown so far that each of the various components of what is termed "the weather" has its own peculiar effect upon permeability. The next step in this investigation would naturally be to expose panels of various compositions until each is evidently "broken down," measuring permeability from time to time. This has been done, and the results are presented on ten charts below. All of the panels involved were not exposed at the same time nor to exactly the same conditions but those reported together were coated at the same time, measured at the same time, and given the same kind and length of exposure as far as practicable. In order to obtain results more quickly the exposure used was severe. Whether the same comparative results would be produced from a milder treatment, only future experiments can tell. The rate of decay of paint and varnish is well known to differ considerably with the kind and degree of exposure. A good paint under favorable conditions will last perhaps six years, while the

part of the year. Such was the exposure by which the results to be tabulated were obtained. No element in it was more intense than that found in actual service. The panels were not subjected to acid fumes, soaking in water, or any other unnatural condition that could be a source of criticism.

To describe this part of the work properly would double the length of this paper. Suffice it now to state that air-tight cylindrical boxes, sufficiently large (7 ft. in diameter, 4 ft. in height), were used, the weathering force emanating from the axes. The exposure used was indeed artificial, but of the same kind as that acting naturally. Rain was imitated with a whirling garden spray; sunlight, by the use of the mercury vapor and tungsten lamps in combination; and cold weather, by admitting the outside air at night. Plenty of ventilation was afforded by use of a fan while the lamps were in operation. The panels were arranged around the sides of the boxes so as to be easily removed or replaced, care being taken to have those of any one comparative set at the same level in the box. Since the lamps could not be located exactly along the axes of the box and in any event mercury lamps do not radiate equally in all horizontal directions, the lamps and panels were rotated along the above axes for different positions with reference to each other from day to day, so that each panel would receive practically its share of exposure. This illustrates one of the many precautions observed in order to secure valid results. From 7 A.M. to 6 P.M., the panels were subjected to a good imitation of a hot, breezy, summer day, the temperature going up to 60° C. for part of the time. From 6 P.M. to 11 P.M. there was rain, and from 11 P.M. to 7 A.M. cold weather.

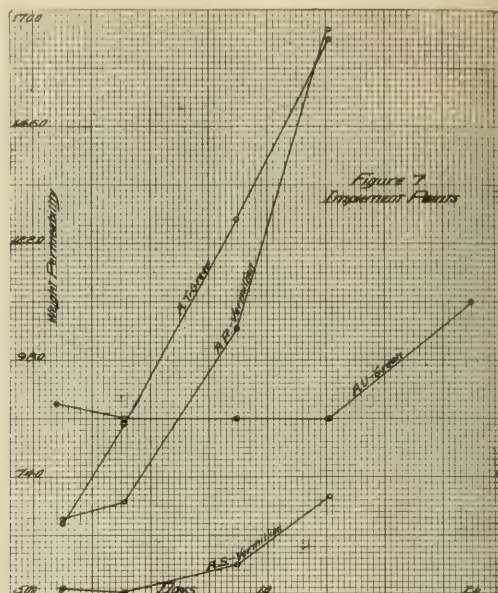
Permeability, of course, is simply one of many indications of paint and varnish decay. Nothing more is claimed for the process being outlined in this article than recognition as an additional method of rating protective coverings. The work is at present

be reported within the proper limits of this paper. Among these should be mentioned the effects of the exposure on several lines of paints for structural iron,



FIG. 6

merely in a preliminary stage and only later studies, which will be prosecuted as rapidly as possible, will demonstrate the real meaning and value of the practical results now to be submitted. The finished



spread over steel panels, and on specially prepared mixtures of lead and zinc with various oils and driers.

RESULTS ON FIG. 7—IMPERMEANT FILMS

	Weight of coat	Meas. No.	Days interval	Permeability		Days interval	Permeability		Days interval	Permeability	
				Actual	By weight		Actual	By weight		Actual	By weight
A R ₁	3.41	1	0	2044	697	2	3	2227	759	3	5 1/2
A R ₂	3.27	1	0	1871	612	2	3	1878	614	3	5 1/2
Average.....	..	1	0	..	654	2	3	..	686	3	5 1/2
A S ₁	2.13	1	0	2374	506	2	3	2323	495	3	5 1/2
A S ₂	2.14	1	0	2428	520	2	3	2357	516	3	5 1/2
Average.....	..	1	0	..	513	2	3	..	505	3	5 1/2
A T ₁	3.29	1	0	2119	697	2	3	2428	799	3	5 1/2
A T ₂	3.08	1	0	1929	594	2	3	2922	900	3	5 1/2
Average.....	..	1	0	..	645	2	3	..	849	3	5 1/2
A U ₁	3.78	1	0	2408	910	2	3	2440	922	3	5 1/2
A U ₂	3.73	1	0	2350	877	2	3	2143	799	3	5 1/2
Average.....	..	1	0	..	893	2	3	..	860	3	5 1/2
A R ₁	4	4 1/2	4515	1540
A R ₂	4	4 1/2	5574	1823
Average.....	..	4	4 1/2	..	1681
A S ₁	4	4 1/2	3360	716
A S ₂	4	4 1/2	3216	688
Average.....	..	4	4 1/2	..	702
A T ₁	4	4 1/2	4365	1436
A T ₂	4	4 1/2	5967	1838
Average.....	..	4	4 1/2	..	1637
A U ₁	4	4 1/2	2553	965	5	7	3121	1180
A U ₂	4	4 1/2	2010	750	5	7	2746	1024
Average.....	..	4	4 1/2	..	857	5	7	..	1102

products of these tests were either purchased in the open market or mixed under the direction of the writer in the laboratory. The composition is based either on published analyses or determinations in the laboratory. The raw materials were of the best grade and had received the "O. K." of the factory chemist, unless otherwise stated.

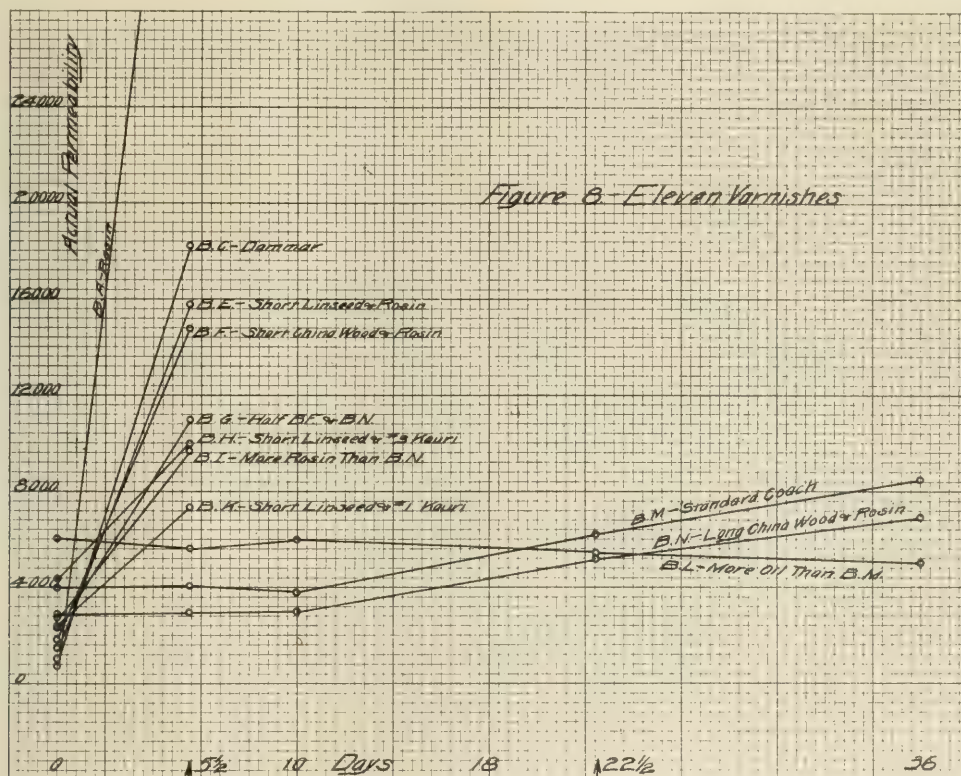
Many interesting results were obtained that cannot

One of the first pieces of work completed was on a line of agricultural paints. The samples were from materials in actual use by manufacturers for the coating of their products. The panels were prepared in exactly the same way with the same material as in the painting of a plow or wagon, all coats being applied at dipping consistency. There was first spread on each as nearly as possible to the same thickness

the ordinary "pink primer" consisting of lithopone and some iron and zinc oxides ground to a paste in linseed oil. All panels were given as a final coat as nearly as possible the same thickness of the same short oil (linseed) No. 1 kauri varnish, so the only difference between the panels, disregarding the above sources of error, consisted in the intermediate coat of vermilion or green. Fig. 7 illustrates the great difference noted, and the numerical results are appended

of actual pores evidenced in the appearance or of a decreased thickness of film. This is borne out by the condition of these panels at the end of the testing period; for it is easy to separate them by their marked difference in appearance. Thus a remarkable contrast is shown between these implement coatings. It would be difficult to believe that A S and A U are not more durable than A R and A T.

The next set of tests to be presented is a group of



below. As in all later diagrams presented where duplicate determinations were made, only average results are plotted.

It will be noticed that where a material has slight durability, as A R and A T, the duplicate with the thinner coating shows the greater change in permeability, as might be expected. In the light of later data, it is justifiable to conclude that all of these panels would have decreased in permeability if the second measurement had been made after a sufficiently short period of exposure, 1 1/2 days being too long. Reasoning now once for all, we conclude that as long as permeability is going down, the rate of oxidation is greater than that of dissolving action, hydrolysis, and decreasing elasticity. But when the latter changes have produced a larger effect than the former, the curve of permeability turns up and the film itself soon goes flat, chalks, checks, or cracks. The rise in permeability would thus seem to be finally the result

of eleven varnishes, embodied in Fig. 8. The actual data are presented herewith:

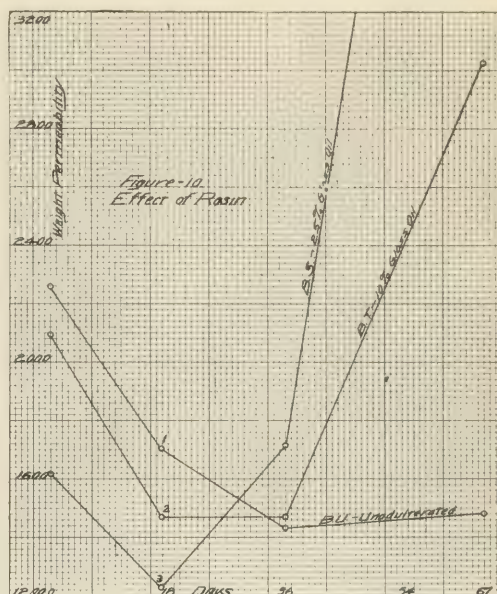
	Meas.	Days	Actual	Meas.	Days	Actual	Meas.	Days	Actual
	No.	interval	per-meability	No.	interval	per-meability	No.	interval	per-meability
B F ₁ ..	1	0	1782	2	5 1/2	15215			
B F ₂ ..	1	0	1898	2	5 1/2	14365			
Ave.	1	0	1790	2	5 1/2	14790			
B E ₁ ..	1	0	1507	2	5 1/2	16064			
B E ₂ ..	1	0	1418	2	5 1/2	15574			
Ave.	1	0	1462	2	5 1/2	15819			
B N ₁ ..	1	0	2978	2	5 1/2	3090	3	4 1/2	3008
B N ₂ ..	1	0	2900	2	5 1/2	2922	3	4 1/2	2916
Ave.	1	0	2939	2	5 1/2	3006	3	4 1/2	2962
B N ₁ ..	4	12 1/2	5816	5	13				
B N ₂ ..	4	12 1/2	4696	5	13				
Ave.	4	12 1/2	5256	5	13				
B G ₁ ..	1	0	2590	2	5 1/2	12612			
B G ₂ ..	1	0	2123	2	5 1/2	9335			
Ave.	1	0	2356	2	5 1/2	10975			
B K ₁ ..	1	0	2465	2	5 1/2	8119			
B K ₂ ..	1	0	2235	2	5 1/2	6578			
Ave.	1	0	2369	2	5 1/2	7348			

Fig. 4 shows a portion of the panel of B R at the end of the test, having a permeability of 2246. While checked up slightly, the major portion of the coating is still left to view. Fig. 5 is a corresponding portion of B P. This panel has a permeability of 5644 and it is evident that little of the original varnish film has withstood the exposure. The differences between these two photographs show that the numerical data upon which these charts are based have real meaning in expressing the condition of the panels.

All of these are standard coach varnishes, except B Q, which is a china wood oil mixture. B O and B P are seen to be running "neck and neck," if we allow for the lack of check panels and for the thinner coating of B O. B R gains its greater durability from its greater oil content. China wood oil makes its best showing in B Q, this being manifestly a fine varnish.

The evil effect of rosin in an exterior paint is well known, though the word "japan" often covers a multitude of such sins in the paint formula. In order to obtain a graphic representation of this evil, a sample of a standard outside white, B U, was divided into three portions. One part was left unadulterated. Ten per cent. of the vehicle by weight was removed from the second portion and an equal weight of gloss oil substituted. In the third portion, twenty-five per cent of gloss oil was similarly replaced. Panels were then constructed and tested. The records of these measurements are now submitted, accompanied by the striking contrast of the curves shown in Fig. 10.

1, 2, 3. In the cases of more durable coatings, it is sometimes possible to arrange the panels in the order of durability long before the measurements are com-



pleted or before any of the films show signs of age.

Fig. 6 gives the appearance of B S, containing 25

RESULTS ON FIG. 10—EFFECT OF ROSIN

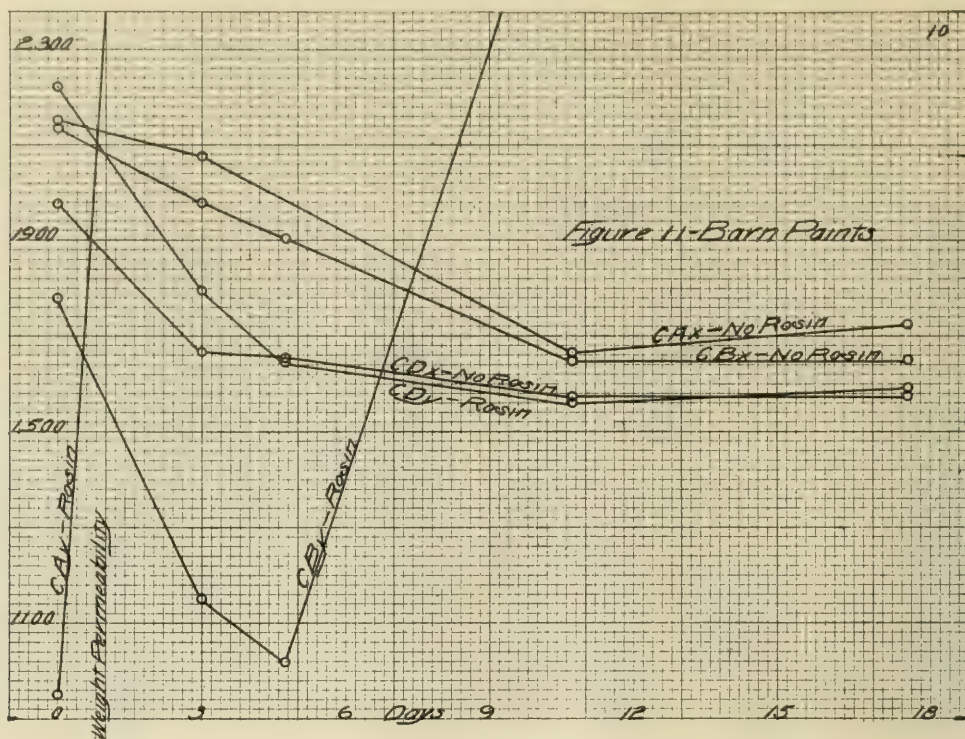
	Weight of coat	Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability	
				Actual	By weight			Actual	By weight			Actual	By weight
B U ₁ ...	14 22	1	0	1623	2308	2	17	1155	1642	3	19	980	1394
B U ₂ ...	14 80	1	0	1491	2207	2	17	1196	1770	3	19	990	1465
Average...		1	0		2258	2	17		1706	3	19		1429
B U ₁ ...		4	31	1004	1427								
B U ₂ ...		4	31	1039	1537								
Average...		4	31		1482								
B T ₁ ...	18 73	1	0	1212	2270	2	17	792	1483	3	19	890	1671
B T ₂ ...	17 62	1	0	1088	1917	2	17	826	1455	3	19	122	1272
Average...		1	0		2094	2	17		1469	3	19		1471
B T ₁ ...		4	31	1667	3122								
B T ₂ ...		4	31	1660	2926								
Average...		4	31		3024								
B S...	13 91	1	0	1163	1618	2	17	883	1228	3	19	1252	1714
B S...		4	31	4559	6341								

The composition of the gloss oil has been already stated. B T, therefore, contains only about 4 1/4 per cent of rosin, while B S contains about 11 per cent. Doubtless the reader will observe that B S appears to fall in permeability more slowly than either of the other materials at first. If a measurement had been made at the end of 5 days, instead of 17, it is believed that B S would have shown the most rapid decrease. It would appear also to be frequently true, if one reasons from all the data presented in this paper, that the smaller the angle of bend plotted at the points of measurement, not beyond the line where the curve first points upward, the sooner will the curve take an upward trend and the coating break down. This is indicated on Fig. 10 by angles

per cent of gloss oil. The film is quite flat and the cracks shown are large. These cracks began after the second measurement. Probably in no line of protective coverings is there so much waste of money as in the so-called barn paints, in spite of their cheapness. In order to develop this point, three liquid paints belonging to this class were made up on different lines, C A, C B, and C D, and each divided into two portions. One portion, marked x, remained untreated, while in the other portion, marked y, rosin in decreasing quantities was incorporated for the several formulas. Thus, C A y has more rosin than C D y, but not more than that found in many commercial barn paints. Duplicate panels were made up for each of the six liquids and the results of their

testing are presented as Fig. 11, with its accompanying tabulation.

In the case of these paints the contrast is evident at a glance. CAy goes to pieces so quickly that



RESULTS ON FIG. 11—BARN PAINTS

	Weight of coat	Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability	
				Actual	By weight			Actual	By weight			Actual	By weight
C Dy ₁	7.81	1	0	2606	2035	2	3	1963	1533	3	13 1/4	1956	1528
C Dy ₂	8.83	1	0	2731	2411	2	3	2332	2059	3	13 1/4	2002	1766
Average.....		1	0	2668	2223	2	3		1796	3	13 1/4		1647
C Dy ₁		4	6	1838	1436	5	7	1891	1478				
C Dy ₂		4	6	1907	1684	5	7	1927	1705				
Average.....		4	6		1560	5	7		1591				
C Dx ₁	7.25	1	0	2817	2042	2	3	2388	1733	3	13 1/4	2351	1704
C Dx ₂	6.76	1	0	2838	1915	2	3	2364	1602	3	13 1/4	2363	1599
Average.....		1	0		1978	2	3		1667	3	13 1/4		1651
C Dx ₁		4	6	2207	1600	5	7	2203	1597				
C Dx ₂		4	6	2283	1543	5	7	2298	1554				
Average.....		4	6		1571	5	7		1575				
C By ₁	9.07	1	0	2035	1846	2	3	1359	1224	3	13 1/4	1205	1093
C By ₂	8.93	1	0	1916	1711	2	3	1206	1077	3	13 1/4	1057	944
Average.....		1	0		1778	2	3		1150	3	13 1/4		1018
C By ₁		4	13	6324	5730								
C By ₂		4	13	5430	4850								
Average.....		4	13		5290								
C Bx ₁	5.32	1	0	3932	2087	2	3	3504	1896	3	13 1/4	3357	1786
C Bx ₂	5.39	1	0	4047	2181	2	3	3637	1960	3	13 1/4	3748	2021
Average.....		1	0		2134	2	3		1978	3	13 1/4		1903
C Bx ₁		4	6	3139	1670	5	7	3098	1648				
C Bx ₂		4	6	3032	1634	5	7	3063	1658				
Average.....		4	6		1652	5	7		1651				
C Ay ₁	6.75	1	0	1415	955	2	3	10905	7360	3	13 1/4	18948	12820
C Ay ₂	6.59	1	0	1438	948	2	3	11715	7720	3	13 1/4	17525	11570
Average.....		1	0		951	2	3		7540	3	13 1/4		12193
C Ax ₁	4.80	1	0	4498	2164	2	3	4116	1975	3	7 3/4	3429	1649
C Ax ₂	4.60	1	0	4659	2143	2	3	4728	2175	3	7 3/4	3660	1684
Average.....		1	0		2153	2	3		2075	3	7 3/4		1666
C Ax ₁		4	7	3526	1692								
C Ax ₂		4	7	3806	1750								
Average.....		4	7		1721								

even the first three days showed a considerable rise in perviousness. C B_y broke down before the fifth day, while C D_y held up until the 6th measurement, and then only is just beginning to pass C D_x, having only a trace of rosin. Attention may be called to the first slopes of these curves as another prediction of the fate of a coating, for C D_y points downward farther than C D_x and bends upward sooner. The

with checks at the end of the test. It must, however, be remembered that the exposure was severe, though there was no rain for the first two days. That in milder weather there would be a great contrast between these two coatings should not be asserted at present.

From the very first it was realized that the severest and indeed final gauge of the value of permeability

RESULTS ON FIG. 20—EXTERIOR ENAMELS

	Weight of coat	Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability	
				Actual	By weight			Actual	By weight			Actual	By weight
E C ₁	5.74	1	0	2168	1246	2	2	2047	1177	3	1	2045	1174
E C ₂	5.75	1	0	2287	1313	2	2	2186	1252	3	1	2125	1218
Average.....		1	0		1279	2	2		1214	3	1		1196
E C ₁		4	13 4	2130	1246	5	8	5017	2880				
E C ₂		4	13 4	2229	1255	5	8	5910	3386				
Average.....		4	13 4		1250	5	8		3133				
E D ₁	8.53	1	0	2536	2162	2	2	2462	2101	3	1	2276	1940
E D ₂	8.65	1	0	2794	2419	2	2	2734	2366	3	1	2539	2195
Average.....		1	0		2290	2	2		2233	3	1		2067
E D ₁		4	13 4	2262	1930	5	8	2161	1627				
E D ₂		4	13 4	2508	2170	5	8	2447	1872				
Average.....		4	13 4		2050	5	8		1749				

same is true notably for C B_y and x. The two curves of C A_x and C B_x are nearly parallel. Investigation showed that the two coatings represented by these have almost the same composition. While in the process being outlined, coatings are judged by what they "do" rather than by what they contain, yet it is apparent that their conduct under the test is a function of their composition.



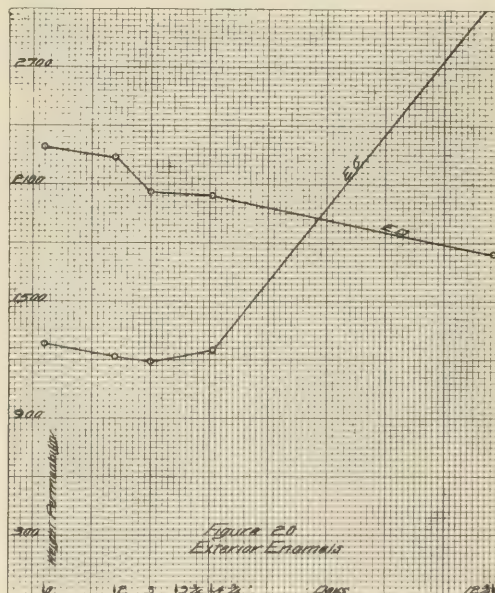
FIG. 14

Fig. 14 is a photograph of panel No. 1 for paint C A_y, which went to pieces so rapidly. The illustration is of its condition after three days exposure. It is checked up even worse than the view indicates.

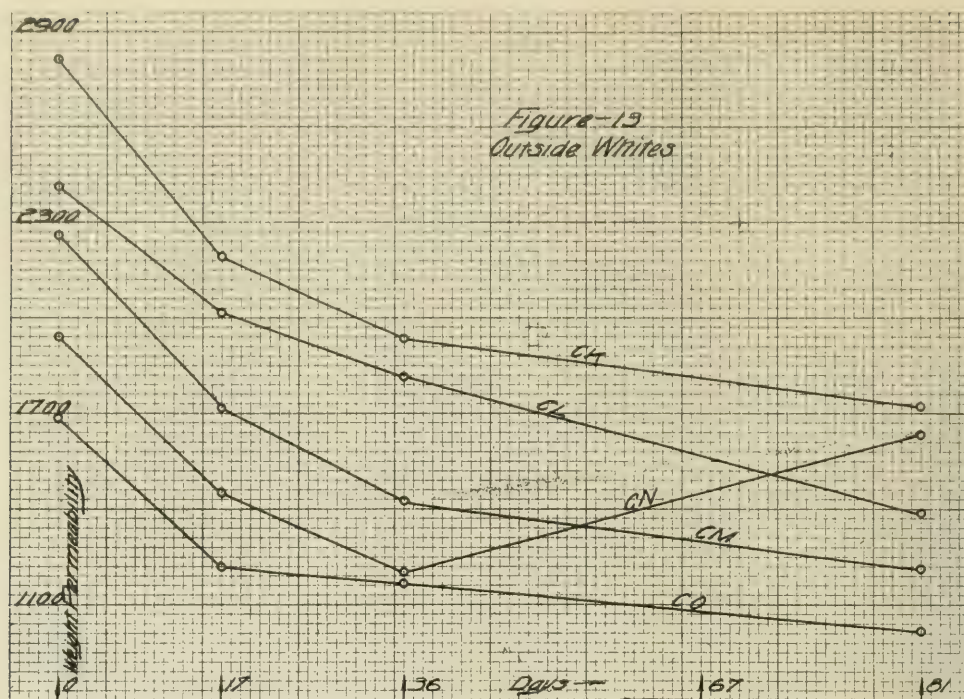
Two exterior enamels were spread on panels in duplicate and tested at frequent intervals for nearly two weeks, at the end of which time they had begun to break down. Fig. 20 and the accompanying table explain the effect of exposure upon them.

The values on duplicates agree very well. E D shows up far better than E C, the latter being covered

as a measure of durability would be upon the best exterior paints. Five representative outside whites were among the first exposed (in duplicate panels) and tested at convenient periods. Fig. 13 is an embodiment of the facts developed in the tabulated permeabilities on page 546:



The composition of these whites corresponds somewhat to their conduct. C K has the highest per cent of lead and of pigment of the five and its curve exhibits next to the greatest bends. One of the panels of C K has a small crack, so that this covering will probably be the second to break down. Generally cracks and checks appear simultaneously on duplicates, and the resulting increased permeabilities agree well. C L contains the highest percentage of



zinc, and its curve has the least tendency so far to turn upwards. C0 is composed of less zinc than CN and possesses a correspondingly greater inclination upwards in change of permeability. CN and CM have about the same composition, and the curves for these are similar up to the thirty-sixth day. Each contains one or more inert pigments but CN holds less zinc and less of the inerts. At the final measure-

ment both panels of CN showed cracks to about the same extent. It is difficult to believe that the explanation for the difference in conduct of these two coatings is to be found in the published analyses. Rather, the writer believes that in the nature of the "japans" used in both cases originates the marked contrast.

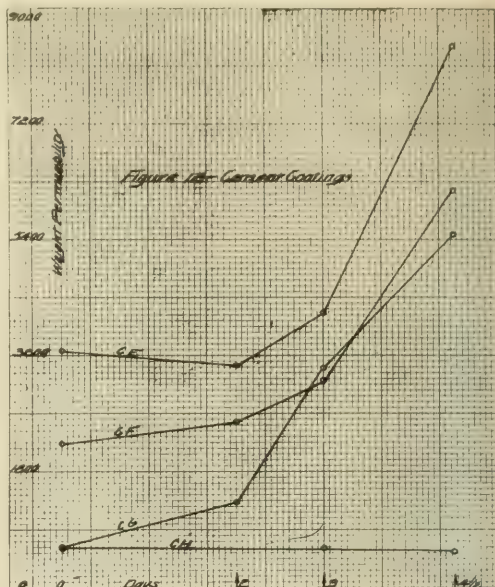
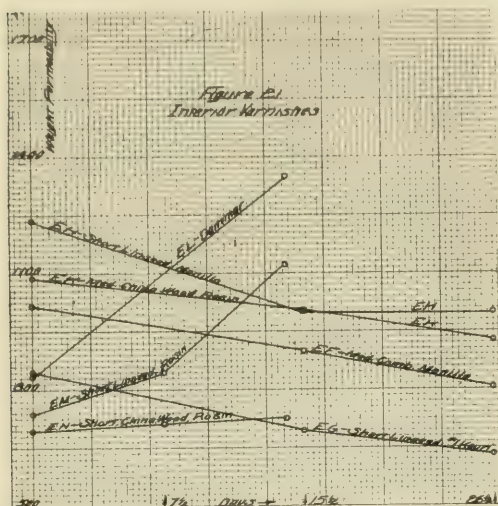
It would probably take six months under present

RESULTS ON FIG. 13—OUTSIDE WHITES

	Weight of coat	Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability	
				Actual	By weight			Actual	By weight			Actual	By weight
C K ₁	22.08	1	0	1466	3237	2	17	1204	2658	3	19	1046	2310
C K ₂	19.41	1	0	1233	2393	2	17	890	1728	3	19	800	1553
Average.....		1	0		2815	2	17		2193	3	19		1931
C K ₁		4	53	900	1987								
C K ₂		4	53	749	1454								
Average.....		4	53		1720								
C L ₁	11.03	1	0	2349	2591	2	17	1961	2163	3	19	1840	2030
C L ₂	11.61	1	0	1922	2231	2	17	1633	1896	3	19	1371	1592
Average.....		1	0		2411	2	17		2029	3	19		1811
C L ₁		4	53	1324	1461								
C L ₂		4	53	1116	1295								
Average.....		4	53		1378								
C N ₁	14.03	1	0	1382	1939	2	17	1054	1452	3	19	867	1216
C N ₂	14.88	1	0	1308	1946	2	17	979	1457	3	19	797	1186
Average.....		1	0		1942	2	17		1454	3	19		1201
C N ₁		4	53	1229	1725								
C N ₂		4	53	1040	1548								
Average.....		4	53		1636								
C O ₁	10.90	1	0	1580	1722	2	17	1204	1312	3	19	1064	1160
C O ₂	10.91	1	0	1520	1658	2	17	1227	1339	3	19	1070	1167
Average.....		1	0		1690	2	17		1325	3	19		1163
C O ₁		4	53	982	1071								
C O ₂		4	53	888	969								
Average.....		4	53		1020								
C M ₁	14.22	1	0	1623	2308	2	17	1155	1642	3	19	980	1394
C M ₂	14.80	1	0	1491	2207	2	17	1196	1770	3	19	990	1465
Average.....		1	0		2258	2	17		1706	3	19		1429
C M ₁		4	53	815	1159								
C M ₂		4	53	844	1249								
Average.....		4	53		1204								

Comparing now Fig. 21 with Fig. 8 and remembering that the former concerns interior and the latter exterior exposure, we see that in general the results are not divergent. The dammar holds up better on the interior, as we should expect. The short line-seed

It has already been observed that among the many possibilities in imitating actual service conditions by the process of testing here presented is the use of



rosin coating in both cases is not so good as that containing china wood oil (E M and E N; B E and B F). E K, the medium combination manila, was not tested with those shown on Fig. 8, but in Fig. 21 it holds its own quite satisfactorily. The No. 1 kauri coating

the same surface for painting as the liquid is designed to cover. In the following results (Fig. 12) obtained on cement coatings, the porous surface used was $\frac{3}{8}$

RESULTS ON FIG. 21—INTERIOR VARNISHES

	Weight of coat	Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability	
				Actual	By weight			Actual	By weight			Actual	By weight
E F.....	3.45	1	0	2716	937	2	15 1/2	2247	775	3	11	2150	741
E F ₂	4.02	1	0	2738	1106	2	15 1/2	2550	1025	3	11	2188	879
Average.....		1	0		1018	2	15 1/2		900	3	11		810
E G.....	3.30	1	0	2566	847	2	15 1/2	2102	694	3	11	1911	631
E H ₁	3.46	1	0	3227	1117	2	15 1/2	2620	907	3	11	2554	884
E H ₂	3.33	1	0	4058	1352	2	15 1/2	3320	1105	3	11	3358	1118
Average.....		1	0		1234	2	15 1/2		1006	3	11		1001
E K.....	3.79	1	0	2876	1089	2	15 1/2	2659	1008	3	11	2437	924
E L.....	4.24	1	0	1568	837	2	14 1/2	2676	1135				
E M.....	4.75	1	0	1553	738	2	7 1/2	1772	842	3	7	2368	1125
E N.....	4.46	1	0	1558	695	2	7 1/2	1615	720	3	7	1634	728

which was broken down in five and a half days on the exterior shows little sign of rising in permeability during twenty-six and a half days on the interior. Thus, some of the history lost in Fig. 8 is now recovered but even here more frequent measurements at shorter intervals would be necessary in order to establish a complete record of the behavior of these varnishes.

inch thick and was composed of 1 part of Portland cement to two parts of sand. The liquids were purchased in the open market, the cans being labeled "damp-proof," "water-proof," "steam-proof," and other like claims. Evidently C E, C F, and C G afford little, if any protection, though C F is the best of the three. C H stands apart from the others, being low in permeability throughout, and justifying

RESULTS ON FIG. 12—CEMENT COATINGS

	Weight of coat	Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability		Meas. No.	Days interval	Permeability	
				Actual	By weight			Actual	By weight			Actual	By weight
C F.....	15.49	1	0	1457	2255	2	2	1663	2578	3	1	2073	3209
C F ₂		4	1 1/2	3980	6165								
C G.....	7.51	1	0	914	686	2	2	1778	1335	3	1	4523	3398
C G ₂		4	1 1/2	7286	5472								
C E.....	8.58	1	0	4293	3682	2	2	4007	3438	3	1	4980	4280
C E ₂		4	1 1/2	9781	8392								
C H.....	9.12	1	0	740	680	2	3	697	635	3	1 1/2	640	58

its water-proofing claims. The data are published simply to indicate the possibilities in some such method for evaluating these coverings.

By the results, C F and C G afford tolerable protection in keeping the water out at first, and through the beneficial valve action previously demonstrated, they will let out all excessive moisture in the concrete beneath. C E, however, is nothing else than a sieve, though it retails at \$1.75 per gallon.

The basal difficulty in the presentation of this paper is a proper selection from the wealth of experimental and speculative material at hand. The question of the mechanism by which water passes upwards through a panel during a measurement of permeability is important, since the same movement occurs in actual exposure, but space does not permit a complete discussion. Certainly on the apparatus, it is in part at least a phenomenon of gaseous diffusion, for the water is in the form of vapor where it touches the film. The far larger portion of work published on diffusion and osmosis has dealt with the gas or liquid, and very little emphasis has been placed upon any view from the standpoint of the membrane. As far as the paint film itself is concerned, it would seem unwise to presuppose a fundamentally different process for the passage of water through it according to whether this happens to be in contact with it in the liquid or gaseous state. Kahlenberg¹ and others have indicated that "semi-permeability" depends on a chemical similarity between the membrane and the solvent, by which the latter dissolves on one side and escapes on the other through a difference in solution or osmotic pressure, the solute, being far less soluble, passing through much less rapidly. It appears to be thus a question of solution, *little though we understand the term*. A variety of experiments are projected to test this point as regards paint films. If such a coating becomes less soluble in water as it dries, the fact would account for the decrease in permeability due to heating or drying, the latter being true.

The writer has further found that continuous contact of a thoroughly dried linseed oil skin with water causes a steadily increasing absorption up to at least fourteen per cent, as shown by increase in weight of the skin. In other words, a condition of equilibrium between liquid water and linoxyn demand a high percentage of water dissolved in the paint film, but as between aqueous vapor and linoxyn, equilibrium would be reached at a lower percentage, varying with the nature of the substance in contact with the vapor and with the vapor pressure. We have in the latter, one of the components of the marked effect of changing temperature on the results obtained by use of the permeability apparatus. During a measurement on the same, we may imagine the coating to be divided up into a large number of layers. The lower layer contains the highest percentage of water, being in contact with the vapor saturated air. The upper layer holds the lowest percentage of water because of contact with air kept at very low humidity.

The actual percentage in both cases will depend on a number of factors, among which is the dissolving power of the coating. Between these two layers there will be a uniform decrease in water content from the lower to the upper, if the affinity for water is the same throughout all layers. These differences in concentration cause corresponding differences in solution tension, resulting in an upward movement of dissolved water through the surface covered and the coating. With gases other than aqueous vapor and membranes other than paint and varnish coatings, the same explanation for permeability as outlined should be postulated, and the apparatus is adapted to such a line of inquiry.

It does not seem necessary to postulate the existence of microscopic or even ultramicroscopic pores in the fresh paint or varnish film, though this theory seems to be generally believed by experts. As the coating becomes thinner through saponification and the resultant formation of more soluble products leaving a chalky upper surface or when it has lost its elasticity and has begun to check or crack, then indeed pores are evidenced by the rise in permeability; the panel has begun to break down.

The foregoing work is believed to be a good start towards an accurate rating of protective coverings. The investigations will be continued by the writer along all lines as rapidly as is practicable with the co-operation of his students and of manufacturers. He desires to express here his thanks to the Patton Paint Company, the Pitcairn Varnish Company, and the Corona Chemical Company for the space in their joint laboratories which has been courteously afforded during this research, and for the stimulating interest and at times assistance of their officials and experts.

MILWAUKEE, WIS.

THE DETERIORATION OF FIREBRICKS DURING SERVICE

By GILBERT RIGG

Received April 15, 1913

The duration of life of a firebrick during service depends upon a multiplicity of factors, physical and chemical, not all of which are by any means understood. These factors may be grouped under three heads, namely:

- (1) The manufacture of the brick.
- (2) The laying of the brick.
- (3) The application of the brick.

Each of these groups of factors has a profound effect upon the value of the other two in determining the life of a brick during service. The third group is to a large extent out of control (but not altogether; for example, carelessness in drying out and starting up a furnace will in many cases shorten the life of the lining). Taking the third group as fixed, then, the problem becomes: How can the other two groups be varied so as to minimize as far as possible the destructive influences in the furnace?

The problem is complicated by the fact that the three groups of factors are controlled by three different sets of men, and to a large extent each of these sets of men understands only the group of factors which he

¹ Jour. Phys. Chem., 10, 141.

controls. If the brick manufacturer thoroughly understood the nature of the effects which his bricks would have to withstand, or if the furnace operator knew what method of manufacture would best meet his conditions, the matter would be a great deal simplified. This desirable state of affairs, however, belongs to a large extent to the future.

Figs. 1 and 2 are photographs of two bricks which

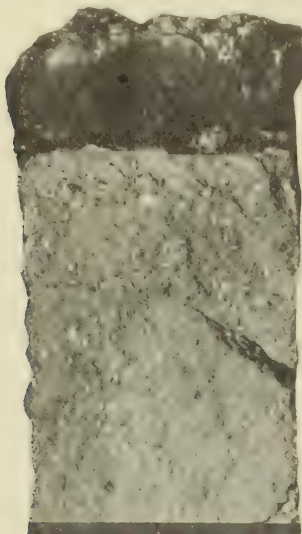


FIG. 1

have been broken across through the layer of slag which has attached itself to one of their surfaces. In Fig. 1, the slag shows a clear line of separation from

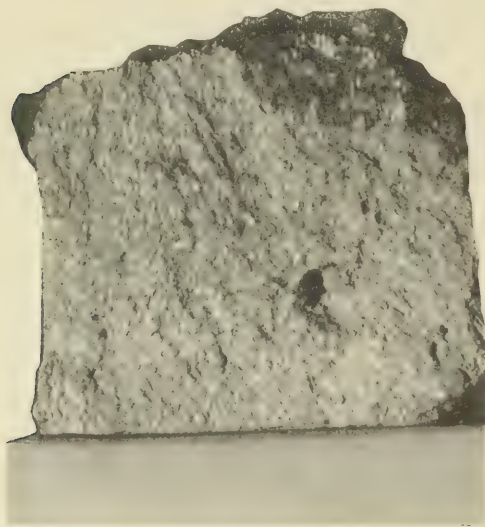


FIG. 2

the brick; in Fig. 2, the slag blends into and penetrates the brick. The first brick will undoubtedly outlast

the second. For this particular purpose brick No. 1 is by far the best article, but I have no doubt that for some purposes brick No. 2 would be perfectly satisfactory. What can be done to standardize brick No. 1 for this particular purpose?

Now I wish at the outset to make perfectly clear that I do not claim to be an expert firebrick maker. I am concerned only with the application of firebrick to certain branches of metallurgy. I have been trying to find out what relation exists between certain types of brick and the duration of life of these brick in certain applications, and the nature of the destructive action which brings about their decay and final failure. Further, I have tried to standardize these types by various tests and methods of examination, and have attempted some work along synthetic lines, to develop masses having certain desirable characteristics. In this paper I am going to define as clearly as I can the destructive influences which I have found to be of paramount importance in determining the life of firebrick and to indicate the type of mass which I have found best fitted to resist them.

I do not propose to deal with such matters as failure by simple fusion of the brick. The remedy for this is obvious. Also within broad lines failure through chemical influences is well understood. Anyone who lines a furnace with silica brick and then exposes it to a strongly basic slag deserves what he gets. I am going to assume that the clay is reasonably well suited both in composition and refractory coefficient for the work it has to do and proceed to discuss its application from that standpoint.

The destructive agencies that come into action in the applications I have been considering may be divided into two groups: (1) Liquid. (2) Gaseous.

DESTRUCTION BY LIQUID MATERIALS (SLAGS, ETC.)

This class of destructive influence is frequently highly effective. Given a refractory mass with pores or openings into which slag can penetrate, it is only a matter of time for the mass to have undergone a more or less complete change in its chemical and physical properties. The extent to which this change may take place, and its effect on the life of the brick depends on certain factors which we shall now consider.

The slag as it enters the body of the brick begins to take up and dissolve fireclay with the result that its temperature of fusion rises. It may happen that by the time the pores of the brick are filled up with slag, or rather a combination of fireclay and slag, the point of fusion of the complex mass is higher than the furnace temperature. This is more likely to happen with dense bricks, of low porosity, than with loose textured ones.

Good examples of this condition are frequently found in spelter retorts. The clay of which these are made will stand a temperature of 1700° to 1800° C., but after being withdrawn from service pieces of clean retort material, free from encrusting slag, may be found to have a fusion point 300° or 400° lower. A thin slice of such a specimen, examined under the microscope, will show numerous cavities, many of which are filled

with slag, and it is doubtless this slag which brings down the fusion point (Fig. 6).

With most, if not all, slags, the vigor of the attack on fireclay appears to be a function of the temperature. Some slags a little above their melting points will lie in contact with the fireclay mass without any serious degree of combination taking place. At a higher temperature, however, the vigor of the attack will increase. The absorption of the fireclay by the slag, as the temperature rises, causes the slag to become more viscous, so that we have the apparent anomaly of the slag stiffening with rise of temperature.

When the slag occurs on the hottest surface of a refractory mass as is the case with a blast furnace lining, the destructive effect is not usually as marked as when the slag occurs on the coolest surface as in a retort or muffle. Under the former conditions the slag as it penetrates into the brick meets with a falling temperature and soon freezes, while under the latter the slag as it penetrates meets with a rising temperature and its destructive effect is enhanced.

What is the remedy for this state of affairs? Clearly with a uniform solid mass free from fissures or pores, penetration would be distributed evenly over the entire surface. Whatever destruction took place would be at the surface. In much of the refractory material on the market, however, this condition does not obtain. The mass is non-uniform, contains numerous fissures and pores and irregular penetration is the rule rather than the exception.

Fortunately it is not a difficult matter to determine on a test piece of a refractory brick what are the prospects of a given molten material penetrating and destroying. For some years I have used the following method, which presents certain advantages.

The size of the test piece may vary within a wide range, from a full-sized block down to a cube $2 \times 2 \times 2$ inches according to circumstances. In any case the surface to be tested for penetration should be a natural surface, not one produced by chipping and grinding unless it is specially desired to try out what would happen under these conditions. As an indication of how a given type of brick would behave under the action of a given flux, the natural skin of the brick should always be used for the testing surface.

The slag should also be made into a cube by crushing fine and working up with a little dextrine and water, or glue. With a 2-inch cube of firebrick, a 1-inch cube of slag should be used. In cutting the firebrick cube care should be taken to reject any specimens when cracks have developed in the test surface due to cutting.

The cube of fireclay is placed in a muffle or crucible with the slag cube on top of it, and the temperature raised to that to which the brick will be exposed in the furnace for which it is destined. The slag melts on the surface of the brick and its relation to the latter can be readily studied after removal from the furnace and cooling.

In some cases it is desirable to use the constituents of the furnace charge, powdered and formed into a

cube, instead of the slag, in cases where the brick will be exposed to these substances rather than to the slag. In all cases there should be careful regulation of the temperature of the test so that it approximates as closely as possible to the working temperature. If the test temperature is too low, an inferior brick may show up well, and if too high, a satisfactory brick may be rejected.

The appearance of the test piece is frequently highly characteristic, and several type cases may be described. It may be pointed out here that the examination of thin slices of the test piece under the microscope frequently affords valuable evidence as to the resistance of the sample to penetration.

Case 1.—The slag has melted and spread over the surface of the brick like an enamel. On breaking the piece across there is a sharp line of demarcation between the slag and the brick, and no staining of the mass, or veins or particles of slag below this line. The line of separation is approximately straight.

This result indicates a low degree of permeability and a high resistance to penetration on the part of the test piece. Microscopic examination should show the particles of fireclay clear and sharp against the slag.

Case 2.—The slag has melted and spread over the surface, and the fireclay next to the slag is stained or semifused, or otherwise altered. Penetrating veins are absent. The dividing line tends to be convex towards the fireclay.

This usually means a combination between clay and slag, and may indicate speedy destruction of the brick. By repeating the experiment one or more times with fresh cubes of slag, using the same test piece of brick, the discolored layer may increase and tend to blend with the slag layer above, the dividing line being obscured and more and more convex downwards. This means that a compound is being continuously formed by the slag and brick whose fusion point is below the working temperature of the furnace. In some cases, however, successive additions of slag simply pile up on the brick and penetration does not increase in depth, indicating that the lower layers of the compound are too infusible at the temperature of the furnace to penetrate further. In this case the brick has a good chance of standing up under the working conditions. This result is rarely seen, except in bricks whose composition is homogeneous and texture fine. With bricks composed of two or more clays, particularly when one clay is in the form of grains imbedded in a plastic bond formed by the other, the two clays will usually resist to a different degree, the bond clay suffering the most, and the discolored layer will approximate in character to the next case.

Case 3.—The slag has melted and spread over the surface and has sent veins into the clay, these veins penetrating more or less deeply into the brick. When the brick is composed of two or more clays as described in the foregoing case, the veins usually penetrate between the grains of the most refractory clays, and after repeating the experiment several times on the same sample the grains of the more refractory clay

will appear imbedded in a fused matrix composed of a combination of the original slag with the more susceptible clay.

This type of penetration is exceedingly common and is responsible for a great deal of firebrick failure. It is commonly supposed, and with a considerable measure of truth, that brick composed of finely ground clays (say through 10-mesh) are more liable to split when heated and cooled than bricks that are coarse-textured (say through 3-mesh). When a finely ground brick gives way under sudden changes of temperature it does so along one or more well marked lines and as a result pieces frequently come off bodily, and the brick is said to spall. It is a mistake, however, to suppose that a coarse-textured brick does not change at all with sudden changes of temperature. Such bricks often do, but owing to their structure, the strain is relieved by a great number of small fissures ramifying through the mass between the coarse, hard grains, but not sufficiently continuous to cause actual falling to pieces of the mass. It is quite common to find old firebricks of this type (and even new ones also) which, if broken¹ with a hammer, allow the coarse grains to drop out of the matrix like loose teeth. The minute fissures or areas of separation between grain and bond, which permit of this disintegration, undoubtedly facilitate the penetration of slags according to Case 3, and lead eventually to failure.

A striking example of the working of this principle is seen in the arches of the zinc oxide furnaces. The under side of these arches is continually bombarded by minute particles of ore from the charge and zinc oxide smoke. A part of these materials adheres to the arch and forms an incrustation called rock oxide, which may reach a thickness of several inches. The furnaces are exposed to great fluctuation of temperature, as the residuum is drawn periodically and a fresh cold charge put in immediately after.

Now actual experience shows that coarse-textured bricks spall under these conditions far more than fine-textured ones. In the former case pieces of rock oxide drop from the arch from time to time with large pieces of brick adhering to them. In the latter case, the rock oxide will come away leaving the brick behind. I have frequently seen large masses of rock come down bearing the imprint of several bricks on its surface of attachment, showing how close the contact had been, and yet little or none of the brick had come away.

In the case of the coarse brick we have always found that the rock oxide had penetrated into the fissures of the brick, separating the grains and solidifying between them. These penetrating veins are continuous with the mass of rock oxide clinging to the arch, and when the weight of this mass becomes too great to be supported it falls, dragging with it a portion of the weakened brick.

Strictly speaking this is not a case of spalling at all. It is a case of rupture under load, the attachment of the load to the interior of the brick being effected by the penetrating veins. The tendency of a fine-grained brick to split and fall to pieces has, I think, been con-

siderably overrated. But it is quite possible to prepare a close-textured brick containing considerable amounts of coarse material, provided that proper care is taken in sizing the grog. The problem appears to me to be very much on the same lines as concrete mixing, and has been discussed at some length by me in a previous paper.¹ In making concrete, care is taken to mix the different sizes of rock, etc., in such proportions that the interstices between the larger fragments shall be filled as completely as possible by smaller fragments, and this result is achieved by first sizing and then mixing the different sizes in definite proportions. By this scheme the amount of cement necessary to fill up the spaces between the pieces is reduced to a minimum.

Consider now the case of a brick made up of a highly refractory nonplastic flint clay, of low shrinkage capacity, and a plastic bond clay. The former is ground to pass, say, a 4-mesh screen, and mixed up to a stiff dough with the latter. The flint-clay being non-plastic is not affected by the water. The bond-clay being highly plastic, takes up the water and forms a plastic mass in which the grains of the flint clay are imbedded.

During the process of drying, the water evaporates and the mass shrinks. The flint-clay takes no part in this shrinkage. On the contrary it resists the shrinkage strongly, forming a sort of skeleton which tends to maintain the dimensions and form of the brick. The loss of volume due to the evaporation of the water, in so far as it is resisted by the flint-clay skeleton, must be taken up by the bond-clay, and in consequence the latter develops fissures and pores.

During burning the mass shrinks still further. If the flint-clay has a low fire-shrinkage, and the bond-clay a high one (and this distribution of properties is common) the bond clay undergoes a further straining and is consequently rendered still weaker and more open-textured than before.

A parallel case may be quoted here by way of illustration. Both firebrick manufacturers and bricklayers agree that poor bricklaying will spoil good fire brick. By poor bricklaying I mean failure to bring the surfaces of adjacent bricks into the closest possible contact. The clay which is used as mortar between the bricks is a very poor substitute for brick. It shrinks a good deal during the drying and burning and becomes fissured and porous. Consequently if wide joints are allowed, either on account of poor bricklaying, or on account of warped and badly shaped brick, the slag rapidly attacks the clay, eats its way between the bricks, and the structure is soon destroyed.

On a much more minute scale this is what takes place in the case of bricks where the bond clay is badly distributed. Just as in the structure, so in the brick, the bond clay should be reduced to the smallest possible amount which will fill properly the interstices between the grains of grog. If a high refractory coefficient is obtained by cutting down the amount of bond clay regardless of this condition we obtain a weak and

¹ *Met. Chem. Eng.*, **8**, 523.

crumbling brick which is readily penetrated and destroyed. The bond should fill the spaces between the grains as thoroughly as the cement fills the spaces between the rock fragments in the concrete, and what is of paramount importance, the spaces to be filled should be cut down to the smallest possible dimensions.

A single example may be quoted from the paper referred to above:

A grog was used giving the following mechanical analysis:

	Per cent
Through 10 on 16	42
Through 16 on 25	22
Through 25 on 30	9
Through 30 on 50	12
Through 50	15

From this another grog was made up:

	Per cent
Through 10 on 16	24
Through 16 on 30	26
Through 30	50

These two grogs were worked up with bond clay and burned at 1100° C. Seven parts of clay were used

and pores. This is borne out by the higher shrinkage of the mass with the sized grog.

Figs. 3 and 4 are photos of thin slices of firebrick magnified 40 diameters. In Fig. 3 the grains of grog have separated from the clay bond, as shown by the clear space surrounding them. In Fig. 4 the adhesion of bond to grog is much closer. I may say that slices of brick are very difficult to prepare as the brick substance has a great tendency to crumble. The specimens usually show numerous cracks and holes in consequence.

Fig. 5 is a photograph of another slice showing a cavity in a brick eaten out and filled by slag. In this case the slag has penetrated into and dissolved and absorbed the brick substance, which shows smooth contours surrounding the slag inclusion.

Steam or hydraulic pressing, and re-pressing help very materially in fortifying brick against slag penetration, by closing up the fissures and pores. Fig. 6 shows a slice of spelter retort which has been made in a hydraulic press, after being in service a month.

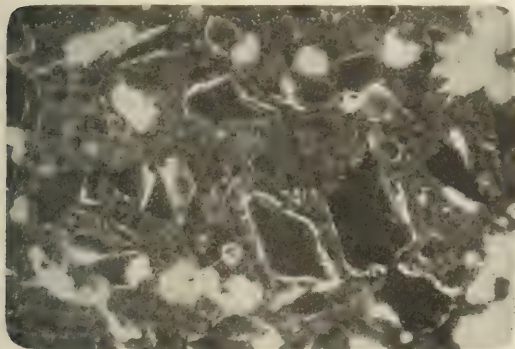


FIG. 3

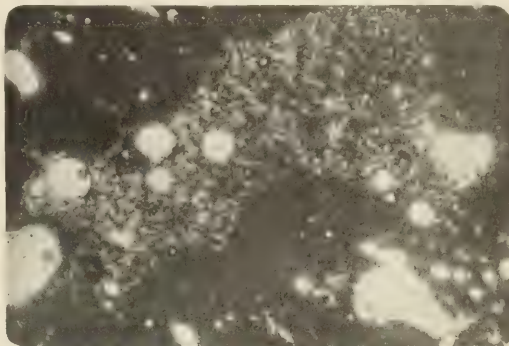


FIG. 5

to nine of grog. The following figures were obtained:

	Original grog	Sized grog
Breaking strain lbs. per sq. in	243	371
Fire-shrinkage, per cent.	4.84	5.44

The gain in strength shows a close adhesion of bond

The contact between the grains of grog and the bond is very close and perfect.

DESTRUCTION BY GASES

This is less general than destruction by liquids but

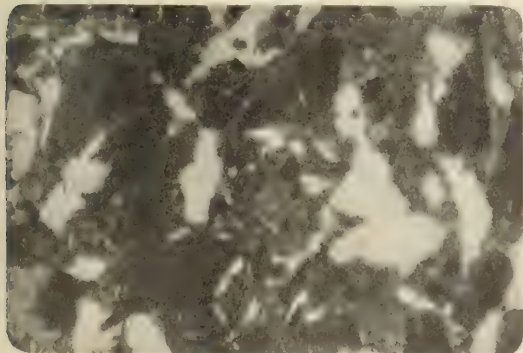


FIG. 4

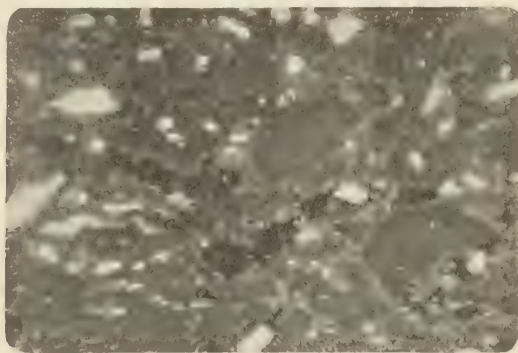


FIG. 6

to grog and greater freedom of the bond from fissures

nevertheless plays an important part at times. With

the exception of hydrofluoric acid gas, direct destruction of firebrick by gas does not occur to any extent. Where gases are primarily responsible for trouble they usually act as conveyors of the destructive influences which are themselves either liquid or solid.

A familiar example is that of salt-glazing. The articles to be glazed are exposed to the vapors of sodium chloride. In contact with the hot fireclay sodium silicate is formed and the chlorine is liberated. If the operation is unduly prolonged the clay is eaten away by the accumulating glaze. A similar action is sometimes met with in furnaces where alkaline chlorides are found in the furnace gases.

A very curious case of firebrick destruction by gases has recently been described by Prof. Osann ("Reduktion und Kohlhung in Hochofen, in Zusammenhange mit Hochofenstorungen," *Stahl und Eisen*, No. 12, 1912). The trouble is usually met with in the top lining of blast furnaces. The bricks weaken and crumble away, more or less rapidly, without exhibiting any sign of fusion. In fact the low temperature at the top makes fusion impossible.

In a case which came under my observation three years ago, the facts were made more striking because, owing to certain furnace troubles, the heat in the top had been excessive and the inner ends of the bricks were burnt hard. The outer ends next the shell appeared to be sheared. They scaled off in laminae, parallel to the shell, and the faces of the laminae were covered with patches of carbon. From the centers of the patches a minute grain could be withdrawn by a magnet. We therefore had the curious phenomenon of the hot ends of the bricks being in good shape and the cold ends destroyed.

Prof. Osann in the paper referred to above explains very clearly what is taking place. It is well known that carbon dioxide in contact with red hot carbon becomes more or less completely reduced to CO, the equation being



The completeness of the reduction to CO is a function of the temperature. At 1000° C. the reduction is practically complete. At 500° C., a temperature frequently met with in blast furnace tops, it is very far from complete.

Now the foregoing reaction is reversible, and in the presence of a catalyst, the reaction proceeds rapidly. The composition of the gas coming from the lower part of the furnace corresponds to a temperature at which the reducing reaction is complete. When the gas arrives at the top, and comes in contact with particles of iron oxide contained in the brick, the reaction reverses and carbon deposits. This carbon accumulates in the substance of the brick until the latter is completely disintegrated.

It is noteworthy that this carbon deposition is particularly noticeable in the bond clay which has been used for laying up the bricks. When an old lining is being taken out it is not uncommon to see masses of brick adhering together and showing, where broken across, the bond clay like a geometrical pattern drawn in charcoal.

A somewhat parallel case of destruction by gas is afforded in the case of blast furnaces running on ores containing zinc. Under these conditions the vapors of metallic zinc are liable to enter the brick and, passing to the cooler parts of the brick, oxidize at the expense of the CO₂ and solidify. The veins of crystallized zinc oxide which result from this action have a powerful effect in rupturing the brick and causing crumbling.

Fig. 7 is a photograph of a piece of the upper inwall lining in which a vein of metallic zinc has condensed.

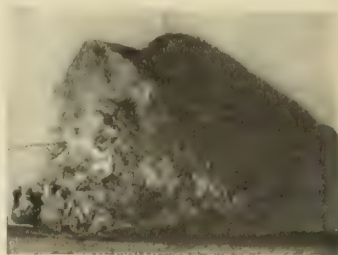


FIG. 7

This is very unusual. As a general rule the vein would be zinc oxide as described above. It is noticeable in these cases of gas destruction that the trouble is set up in the interior of the brick, and in the clay bond in which the bricks were laid. It is by no means confined to the surface; moreover, if the bricks were entirely impenetrable the destructive effects could not occur. The effect is one of penetration by the destructive influences much as in the case of destruction by slags.

Other things being equal I am convinced that the more compact and close-textured a brick is, the better it will stand up against corrosive slags and gases. And the truer it is to shape, the closer it can be laid up in the work; penetration into the bond between the bricks is facilitated by wide joints and is highly destructive to the work. As regards the risk of spalling with changes of temperature in the case of close-textured brick, experience shows that brick of this type can be made to stand up perfectly. If they spall, the trouble is due to unsuitable clay, or poor workmanship, or both.

RESEARCH LABORATORY
NEW JERSEY ZINC CO.
PALMERTON, PA.

THE INFLUENCE OF CINDERS ON THE CORROSION OF IRON IMBEDDED IN CLAY¹

By WALTER B. SCHULTE

Investigations of electrolytic corrosion of underground structures occasionally reveal examples of marked corrosion under certain conditions which preclude a consideration of stray currents from electric railways as the cause. Filled ground seems to be especially harmful to iron pipes, especially where the filling is composed largely of cinders, coal, and furnace products.

Of the various explanations which have been offered, to account for this corrosion the more common are:

¹ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

that the sulfur, which is a constituent of most coals, probably forms sulfuric acid, with the resultant chemical corrosion; also that cinders and particles of conductive carbon in contact with iron produce a local couple, and the pits which are formed are attributed to this effect.

The objection to the former theory is that after a severe heat treatment the sulfur is usually expelled from the cinder material, and that the latter explanation is not completely adequate is indicated by the fact that the corrosion occurs even where there may be an intermediate layer of clay between the cinder bed and the pipe. Certain cases of deep pitting of iron pipe have been called to the attention of the writer where an overlying bed of cinder filling out of direct contact with the pipe seemed to be in a measure responsible for the damage noted.

It is well known that if a mass of carbon and a mass of iron are imbedded in an electrolytic conductor, such as in moist earth, a difference of potential is established between these two bodies, the iron being electrochemically positive to the carbon. This potential does not establish a flow of current unless metallic contact is made between these two bodies. While a layer of carbon material may be separated from an iron pipe in one locality by a bed of sand or clay, corrosion may be produced at that locality by reason of contact between the iron and the carbon bed at some other position, such for example as occurs where a service pipe or other portion of the underground system may pass through the carbon bed. It is evident, therefore, that contact between the cinders and the iron is not necessary at the exact location where the corrosion is observed in order to account for such corrosion.

An active couple produced by carbon and iron results in the iron being the anode and the carbon being the cathode. Polarization tends to reduce the flow of current but this polarization is minimized if air has ready access to the carbon bed; therefore the nearness of the carbon bed to the surface of the earth is a factor which influences the corrosion caused by such material.

The object of the investigation here described was to reproduce, in the laboratory, conditions which were found in the field and to make laboratory measurements of potential and current flow, and determination of the amount of corrosion. The experiments were carried out in the Chemical Engineering Laboratories of the University of Wisconsin.

APPARATUS

The apparatus, as set up in the laboratory, included a sheet of iron buried in a bed of clay on the top of which rested a layer of granular carbon which represented the cinder bed. Electrical contact between the plate and cinders was provided for by a wire connected between them. The arrangement of the apparatus is shown in Fig. 1.

It is of course evident that the conductive layer of carbon here used has a higher electrical conductivity than that produced by cinder filling, as found in practice, and the reason for using this was to accelerate

the action so as to produce measurable results within a short time.

The iron plate was of No. 24 sheet iron which was pickled, dried and weighed before being placed in the clay which was taken from a fresh excavation and was moist when placed in the box. The layers below and above the plate were well tamped in place. The carbon, which had been used as a resistor in electric furnaces, was granular, the particles ranging from $\frac{1}{4}$ " to $\frac{1}{2}$ " in diameter. A graphite block, with a stem, was placed in the carbon to make electrical contact between the carbon and external connections, and insulated wire connected to the plate was brought out through the clay. The carbon lead was connected to a switch, also connected to the iron plate terminal

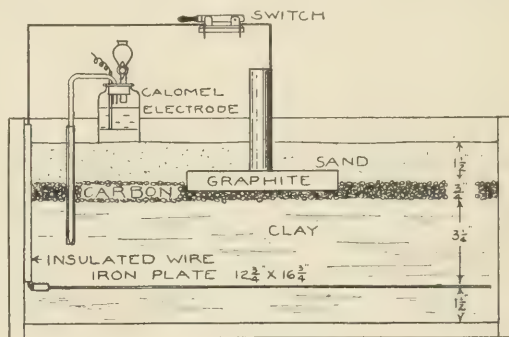


Fig. 1

so that by closing it the cell was short-circuited. The switch was provided with short leads so that an ammeter or voltmeter could be connected to them and measurements be made with the switch open. The carbon was covered by a $1\frac{1}{2}$ " layer of sand at the beginning of the test but this was removed on the fourth day.

To measure the single potentials of the iron and carbon against the clay a calomel electrode was employed with a long nose reaching down through a glass tube into the clay half way between the carbon and iron. A few drops of normal KCl were poured into the bottom of the glass tube to moisten the clay and assure good contact between the clay and electrode.

MEASUREMENTS

Before closing the switch, the potentials of the iron and carbon against the clay were determined by the potentiometer method, taking -0.56 volt as the potential of the calomel electrode. The results are given below:

Total E. M. F.,	0.842 volt, carbon cathode
Clay to carbon,	-0.638 volt
Iron to clay,	$+0.204$ volt

Total, 0.842 volt
A voltmeter indicated 0.83 volt.

After making the single potential measurements, the circuit was inadvertently closed for a minute or two, after which the voltage, as indicated by a voltmeter, had fallen to 0.72 volt. Further short-circuiting caused the voltage to drop from 0.68 to be-

tween 0.45 and 0.56 after a few minutes. One and one-half minutes after opening the switch the voltage increased to 0.68 volt.

The cell was short-circuited for twenty minutes and the switch then opened, after which single potential measurements were made at various intervals.

After being on short-circuit for seventeen hours, similar single potential measurements were made, during which time the average current, as measured by a milliammeter, was 0.0515 ampere. The data of these measurements, as tabulated in Table I and plotted in Fig. 2, show that the rate of depolarization is decreased after the cell has been short-circuited for the longer time.

The cell was then allowed to stand short-circuited and readings were made of the voltage and current at various times during the run, the results of which are tabulated in Table II. The instruments were of standard make and in good calibration and of the following scales and resistances:

Voltmeter 0-15 volt; 53.5 ohm resistance
Ammeter 0-500 mil ampere; 0.09 ohm resistance

During the fourth day the layer of sand above the carbon was removed as noted in the table. The

TABLE I—DEPOLARIZATION

Single potentials of carbon				Single potentials of iron			
Short-circuited 20 minutes		Short-circuited 17 hours		Short-circuited 20 minutes		Short-circuited 17 hours	
Time Min.	E. M. F.	Time Min.	E. M. F.	Time Min.	E. M. F.	Time Min.	E. M. F.
1	-0.432	1	-0.394	0	+0.184	0	+0.162
2	-0.478	1 1/2	-0.424	1 1/2	+0.184	1	+0.160
3	-0.485	2	-0.434	2	+0.186	2	+0.160
4	-0.508	3	-0.438	3	+0.180	3	+0.160
5	-0.510	4	-0.442	4	+0.182	4	+0.160
6	-0.516	5	-0.452	5	+0.180	5	+0.160
7	-0.524	8	-0.452	6	-0.178	8	+0.158
10	-0.530	10	-0.458	24	+0.180	10	+0.158
24	-0.540	16	-0.468			16	+0.158
42	-0.564	23	-0.470			23	+0.156
		43	-0.474			43	+0.156
		60	-0.484			60	+0.158
			-0.499				

clay began to dry out, so that beginning with the tenth day about half a liter of water was sprinkled over the carbon and allowed to soak in before a set of readings were made. No readings were taken between the 33rd and 58th days, nor was the cell moistened, with the result that the current on the 58th day was almost nil, and the potential 0.22 volt. Three minutes after the cell had been moistened the observed values increased to 0.0175 ampere and 0.32 volt.

Rough integration of the curve plotted between current and days, with the current as zero on the 58th day, gives 35 ampere hours. If the cell had been moistened regularly each day throughout the test it is fair to assume that the average current would have been 0.03 ampere: 0.03 ampere for 58 days is equivalent to about 42 ampere hours. The average voltage over this period can be taken as 0.35 volt.

The interesting point to be noted is that as long as the clay was moist a current flowed continuously

from the iron to the carbon, the depolarization, due presumably to the action of the air on the carbon, taking place at a constant rate.

The loss of iron by one ampere-year is about 20 pounds so that 0.03 ampere, the assumed average current with the clay moist, would be about $20 \times 0.03 = 0.6$ pound.

The area of the plate was 1.45 square feet or 2.9 feet total surface, so that the theoretical corrosion per square foot would be 0.23 pound per year or about

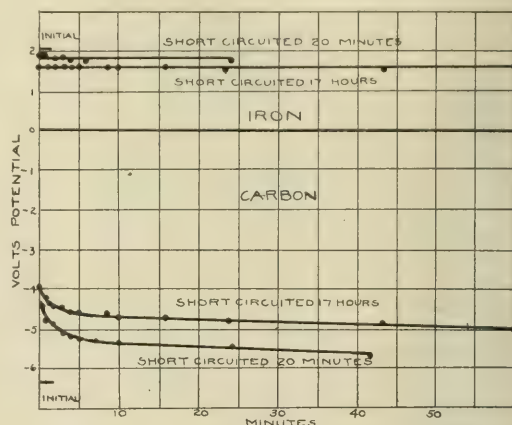


FIG. 2

$\frac{1}{4}$ pound per year. The loss of $\frac{1}{4}$ pound per foot from each surface of a plate would destroy the equivalent of a No. 30 sheet in one year or half of a No. 24 sheet. If this corrosion were concentrated in six square inches area on every square foot, the metal would be pitted to the depth of 0.15 inch which would pierce a three-inch cast iron main in a little over two and one-half years.

TABLE II—CURRENT AND VOLTAGE READINGS

DAY	AMPERE	VOLT	REMARKS
1	0.052	0.45	
2	0.0518	0.50	
3	0.050	0.45	
4	0.051	0.45	Sand removed from top
5	0.051	0.44	
7	0.0495	0.38	
8	0.035	0.40	
9	0.030	0.20	
10	0.040	0.40	Began wetting
11	0.035	0.40	
12	0.0475	0.42	
14	0.0475	0.42	
15	0.040	0.42	
17	0.041	0.40	
24	0.030	0.35	Dried out since last reading
25	0.0375	0.36	
29	0.023	0.30	
30	0.020	0.20	
31	0.035	0.40	
32	0.028	0.35	
33	0.028	0.35	
58	0.015	0.32	

CORROSION OF PLATE

After the 58th day the cell was dismantled. Examination of the clay near the plate showed that the rust had penetrated into it as much as $\frac{1}{4}$ inch in some places. The plate was spotted with oxide

and greenish iron compounds. Corrosion was noticed both on the upper and lower sides of the plate and the corner diagonally opposite the wire connection was eaten through.

The plate was washed, the greater part of the rust scraped off and the remainder then dissolved off by hot ammonium citrate, after which it was weighed. The data follow:

	Grams
Weight of plate before test.....	401.6
Weight of plate after test.....	346.5
Loss.....	55.1

Thirty-five ampere hours theoretically would corrode 36.4 grams of iron so that the efficiency of corrosion in this case would be about 150 per cent.; that is, it may be said that two-thirds of the loss by corrosion was due to the current produced by the difference of potential between the carbon and the iron.

These experiments were intended as preliminary work for further investigation, which, however, was not undertaken, but a description of this first, rather incomplete work, it was thought, would prove of interest and draw attention to the influence of carbon and cinders on the corrosion of iron and perhaps lead to further experimentation on the subject. Further work along this line should be undertaken with the conditions more closely approaching those actually found; that is, using cinders instead of carbon and putting them, with the iron plate, in the earth. Similar plates not connected with the carbon should also be buried so that the amount of natural corrosion can be determined. Under these conditions, with the higher resistant cinders, it is to be expected that less current would be produced.

An interesting case of corrosion of a gas pipe which may be explained by action similar to that discussed above has been observed recently by the writer. Along a certain street the gas mains were paralleled by a water main buried a short distance beneath. The soil is mainly clay or silt but at the lowest portion of the street the water main dipped into a peaty layer. The gas main lay in the clay above the peat at this point and was corroded through at several places. The main apparently was in a locality not subjected to stray currents from the street railway or grounded power circuits so that the currents causing the corrosion must have come from other sources.

A length of gas main about 400 feet long was disconnected from the adjoining portion. Potential measurements between this disconnected length and an iron rod driven in the black layer showed that the gas main was 0.3 volt positive, and readings between gas and water connections showed that current was flowing from the gas to the water main through the earth. The corrosion can be explained by the fact that peat sets up a different potential toward an iron surface than does clay, and connections between the gas and water services on the consumer's premises makes the couple electrolytically active, thereby producing electrolytic corrosion.

RECENT ANALYSES OF THE SARATOGA MINERAL WATERS. III

By LESTER RUSSELL MILFORD

Received April 5, 1913

ACQUISITION OF THE GENERAL CARBONIC COMPANY

Following the passage of the "Anti Pumping Act" in 1908, by the legislature of the State of New York, the gas companies situated at Saratoga Springs, which were pumping the mineral water and extracting the gas from it for commercial purposes, were the defendants in a great amount of litigation. One of the largest gas-producing companies was known as the General Carbonic and was situated in the Geysers district. This company derived about one-half of its supply from one spring with natural flow (the Adams) and the remainder from several wells by pumping. This plant continued its operations until the Reservation Commission, in July, 1911, acquired the property which contained about one hundred



ISLAND SPRING.

acres of land and 25 existing bores, of which 19 varied in depth from 270 to 533 feet to the bottom of the well. This acquisition was necessary for the control of the large area of the mineral water basin, adjacent to the fault from which the wells and springs have their origin. In order to obtain all of the information possible relating to the condition of the wells upon this property and the effect of pumping on this land and the lands of other proprietors arrangements were made for taking scientific observations while the previous operations of this company were continued without disturbing existing conditions. The General Company continued pumping from July 2, 1911, to July 20, 1911. During this period six pumps worked continually, pumping from wells ranging from 316 to 397 feet in depth, an average of 120,000 gallons of water in twenty-four hours.

Observation of water levels, flow of water, gas pressure, and other physical conditions were noted. Com-

plete chemical analyses of the waters and frequent chlorine and alkalinity determinations were made. On July 20, 1911, the pumping was stopped and since then there has been a constant recovery of the mineral water basin and a rise in water levels of from 80 to 150 feet. A mass of information was thus obtained which showed the effect of pumping, the degree of depletion of the mineral water basin, and the

produced too many outlets of gas and mineral water and in order to conserve the springs it became necessary to check the flow of some of them. A number of wells which showed no energy were packed with clay while those exhibiting signs of life were tubed and allowed to "spout" or else capped temporarily.

The property on which these springs and wells are located is situated east of the Delaware and Hudson Railroad tracks, along the valley and banks of the Coesa Creek. The limestone, from which the springs emerge, is found here at a depth of 275 feet covered with a layer of shale rock of about 200 feet thick, and this covered with a layer of clay 40 to 60 feet thick and this in turn buried beneath a deposit of about 15 feet of gravel. The steep and wooded banks of the Coesa Creek, which flows through this property for nearly a half mile, furnishes unusual opportunities for park development. Several paths, roads and bridges have been built here to enable visitors to enjoy the whole landscape and visit all of the springs.

	1	2	3	4	5
	Adams Spring	Ditch Well No. 2	Flat Well No. 2	Island Spring	Pump Well No. 4
Date of analysis 1912	3/20	9/19	10/19	10/23	7/18

RESULTS IN MILLIGRAMS PER LITER
IONS, RADICLES AND OXIDES AS ACTUALLY DETERMINED

SiO ₂	8.95	73.55	56.55	10.05	9.20
SO ₄	2.30	5.35	2.88	8.23	7.52
HCO ₃	3983.76	2015.11	4514.67	3242.40	1799.21
NO ₃	0.17	trace	trace	0.18	trace
NO ₂	trace	trace	trace	trace	trace
PO ₄	none	none	none	none	none
AsO ₄	none	none	none	none	none
BO ₂	trace	trace	trace	trace	trace
Cl.....	3842.86	1282.60	4230.77	2649.48	894.85
Br.....	42.28	3.41	26.26	16.37	6.82
I.....	4.20	0.31	1.45	0.76	1.07
Fe.....	8.85	9.19	244.96	6.93	5.09
Fe and Al.....	10.65	21.77	315.28	10.96	10.56
Al ₂ O ₃	3.30	23.72	132.59	7.60	10.30
Mn.....	none	none	trace	trace	trace
Ca.....	670.00	378.81	689.01	586.80	350.56
Mg.....	252.60	214.13	249.27	202.96	83.36
Ba.....	10.35	1.18	6.59	6.00	3.76
Sr.....	trace	none	1.53	1.34	trace
K.....	250.70	42.32	279.34	231.71	82.11
Na.....	2556.52	711.87	2782.14	1717.99	640.98
Li.....	7.43	2.35	5.21	4.53	0.97
NH ₄	9.82	2.18	19.27	11.40	2.88
Oxygen to form Al ₂ O ₃ ..	1.50	11.14	62.27	3.57	4.84

HYPOTHETICAL FORM OF COMBINATION

Formula					
NH ₄ Cl.....	51.12	6.48	57.13	33.82	8.54
LiCl.....	44.87	14.27	31.63	27.47	5.87
KCl.....	438.01	77.50	508.48	426.84	149.88
NaCl.....	5892.90	1802.89	6470.17	3958.48	1339.84
KBr.....	62.00	5.00	38.50	24.00	10.00
KI.....	5.50	0.40	1.90	1.00	1.40
Na ₂ SO ₄	3.40	7.91	4.26	12.17	11.13
NaBO ₂	trace	trace	trace	trace	trace
NaNO ₃	0.23	trace	trace	0.24	trace
NaNO ₂	trace	trace	trace	trace	trace
NaHCO ₃	869.61	...	859.14	572.04	403.41
Ba(HCO ₃) ₂	19.56	2.22	12.44	11.33	7.14
Sr(HCO ₃) ₂	trace	none	3.66	3.66	trace
Mg(HCO ₃) ₂	1533.00	1008.71	1499.91	1221.22	505.99
MgCl ₂	182.43
Ca(HCO ₃) ₂	2713.50	1531.73	2786.01	2372.74	1419.77
Fe(HCO ₃) ₂	28.14	29.27	780.11	22.07	16.20
Mn ₂ O ₄	none	none	trace	trace	trace
Al ₂ O ₃	3.30	23.72	132.59	7.60	10.30
SiO ₂	8.95	73.55	56.55	10.05	9.20
Residue on evaporation dried at 105° C.....	9668.00	3952.00	11572.00	7116.00	3007.00
Total solids in solution (computed).....	11654.09	4766.08	13242.48	8704.73	3898.67
Temperature.....	10° C.	(a)	10.5° C.	11° C.	(a)

(a) = not taken.

1, 2, 3, 4, 5 Files N. Y. State Dept. of Health.

progress of recovery from such depletion. That there is a close underground connection of all these springs has been made clear by these experiments. In a few weeks' time several wells and springs on the General property became active and wells, formerly pumped, became natural spouting springs. These



ADAMS SPRING

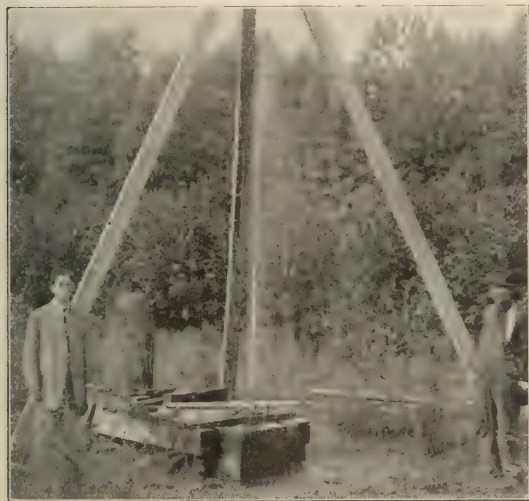
The Commission is in hopes of bottling some of these waters, and experiments are now being conducted to determine the fitness of Pump Well No. 4, Flat Well No. 2 and the Island Spring for this purpose.

DESCRIPTION OF THE WELLS AND SPRINGS

The Adams Spring, which has been flowing since it was drilled in 1904, is situated in the Geysers district, on the high embankment rising from the Coesa Creek, being just south and above the Champion Springs and the Clark Well No. 2. It is about one-quarter of a mile northeast of the Coesa Spring and on the opposite side of the Delaware and Hudson Railroad tracks. This spring is 344 feet deep and has a flow of about 10 gallons per minute. It has a large excess of gas, each volume of water giving 4 1/2 volumes of gas, and furnishes approximately 1200

pounds of gas in 24 hours. The waters of the Adams Spring are strongly mineralized and approach very closely to those of the Coesa. This spring is one of the best in the group, but it has not been developed except in connection with the gas industry of the General Carbonic Company.

The Ditch Well No. 2 is a shallow surface well and does not penetrate the rock. In drilling the well a large boulder was struck at about 45 feet below the surface and the tubing was driven to that depth. This well is situated in the bed of a ditch in the Coesa valley about 40 feet east of the creek and 200 feet south of the Pump Well No. 4. It was drilled in 1896 and has a very small flow averaging about one quart per minute. The water is moderately mineralized, resembling that of the Emperor. The analysis of this water shows the presence of magnesium chloride. This substance has been reported¹ only twice before in the published analyses of Saratoga waters. As a great amount of chemical and geological data have been published and various theories have been advanced to account for the origin of these waters,²



FLAT WELL No. 2

this presence of magnesium chloride in a shallow well will be interesting to the geologists familiar with this region.

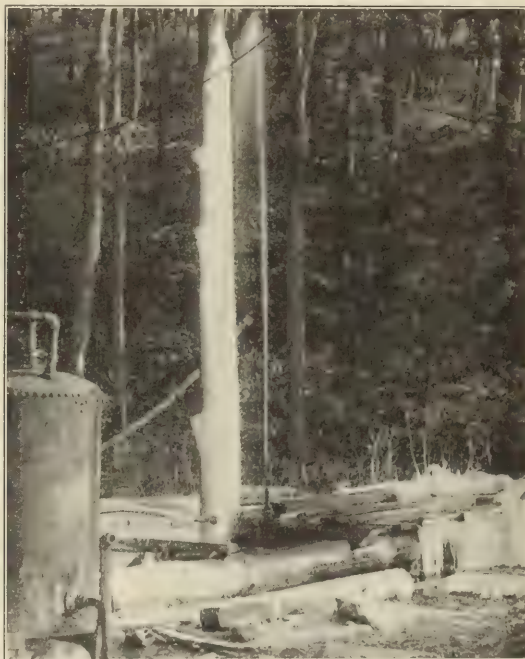
Flat Well No. 2.—This well is situated across the Coesa Creek southwest of the gas company's plant beside the road leading to Ballston Ave. and the Coesa Spring. It is located in the flat land along the Coesa valley and was pumped for the gas. It was drilled in 1904 and is 385 feet deep. When first drilled it had a flow at times of 8 gallons per minute but for a long time previous to its purchase by the Reservation Commission it showed no signs of water. In August, 1912, the well was retubed and immediately

¹ J. R. Chilton, Washington Spring, 1843; Dr. C. F. Chandler, Imperial Spring.

² "The Mineral Springs of Saratoga," N. Y. State Education, Dept. Museum, Bull. 169, 1912, by James F. Kemp

developed into a "spouter," throwing a large stream of water accompanied by great volumes of gas many feet into the air. It shows a static pressure of 42 pounds on the gauge fastened at the top of the casing. The water is strongly alkaline-saline, having a high sodium chloride, alumina, and calcium, magnesium, and iron bicarbonate content. It is unusually high in iron and alumina and shows a natural water containing a large amount of colloids. This water may be termed a natural chalybeate water and is at the head of all known waters of this class in point of strength.

The Island Spring is located on a small island in the bed of the Coesa Creek just below the dam. It was drilled in 1901 and is about 400 feet in depth. This was formerly used as a gas well with no flow of water. In four months after the cessation of pumping, the Island Spring began to overflow with mineral water for the first time in its history. It now has a flow of eight gallons per minute, and spouts many



PUMP WELL No. 4

feet into the air. The water is strongly mineralized and is charged with an abundance of gas. It is an alkaline-saline water and averages with the Hathorn No. 1.

Pump Well No. 4, formerly known as Hathorn Purchase No. 1, is situated on this same tract of land along an abandoned tail race. It was drilled in 1899 and is 350 feet deep. When this spring was first used for gas it had a large flow but it soon ceased and had to be pumped. A short time after the shutting down of the pumps of the General Carbonic Company, this well developed into a picturesque "spouter" and now gives excellent mineral water at the rate of

11 gallons per minute. The water of this spring is suitably mineralized, being of the mild saline-alkaline class and is the nearest approach to a table water of any.

During the summer of 1912 many of these waters were examined for radium and thorium. Samples of the water were collected and sent to Washington, D. C., where they were tested. The field work of the gases was performed by Dr. R. B. Moore, of the Bureau of Mines, Department of the Interior, a noted authority on radioactivity. His report will probably occur in a future bulletin by him. Sanitary analyses of these waters were made and the results showed free and albuminoid ammonia content with low nitrites and nitrates. No bacteriological examinations have yet been made.

The writer is indebted to John C. Minor, Jr., Secretary of the General Carbonic Company, for information concerning these wells. I also wish to acknowledge the assistance given by Herbert Ant, of this laboratory, who helped me in some of the analyses.

REFERENCES

Proceedings Supreme Court, Saratoga County, Hathorn vs. Strong, March 15, 1907.

Report of the Commissioners of the State Reservation at Saratoga Springs, 1912, 1913.

STATE HYGIENIC LABORATORY
ALBANY, NEW YORK

THE PRECIPITATION OF GOLD BY MANGANOUS SALTS¹

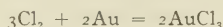
By A. D. BROKAW

Received April 14, 1913

Some interesting occurrences of gold associated with manganese dioxide led to the suspicion that manganous salts, under certain conditions, might react with solutions of gold salts to bring about a mutual precipitation: the gold in the free state and the manganese as hydrated manganese dioxide. A search for literature on such reactions was without avail, and experiments were undertaken with a view to ascertaining if such a reaction is possible, and if so, under what conditions it can take place. The reaction in question is in a sense the reverse of the series of reactions involved in the well-known "chlorination process" of extracting gold from its ores:



and



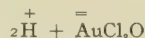
The reaction is doubtless much more complex than the summary equations, but it will be seen that a reversal of the series would lead to the formation of gold and manganese dioxide.

Auric chloride solutions of varying concentrations were mixed with solutions of manganous chloride with concentrations ranging from 0.5 *N* up to saturation, but no reaction was detected even when the mixture was boiled for several minutes. The addition of a very small amount of alkali to the mixtures, in the cold, caused an immediate precipitation of a dark brown mass resembling manganese dioxide in the hydrated form commonly precipitated. The precipi-

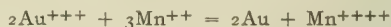
tate was collected, carefully washed to free it from the gold solution, and then treated with standard oxalic acid, containing a small amount of sulfuric acid. The solution thus obtained was divided into equal portions: one was analyzed for manganese and the other titrated for loss of oxalic acid. The results showed that for every equivalent of manganese an equivalent of oxygen had been taken up by the oxalic acid, proving the precipitate to be manganese dioxide. In a check experiment the precipitate was taken into solution with the standard oxalic-sulfuric acid mixture, which was titrated for loss of acid. The manganese in solution was then reprecipitated as hydrated manganese dioxide by a standard method, and the precipitate was again treated with the standard acid mixture. The same loss of acid as before showed the original precipitate to be manganese dioxide.

Gold was left by the solution of oxalic acid and was readily recognized as such.

Gold chloride solutions are notably acid in their reaction, due probably to hydrolysis in part, and in part to the ionization of an addition product with water. Hittorf and Salkowsky showed by electrolytic experiments that gold chloride solution is ionized as follows:



Solutions of gold chloride show marked acid properties toward indicators, and apparently the acidity thus developed is sufficient to suppress the reaction,



If we postulate the intermediate formation of MnCl_4 in minimal amounts, we are justified in assuming that the salt would be largely hydrolyzed, since tetravalent manganese is a very weak base. This hydrolysis would be suppressed by the presence of acids, but on reducing the acidity, hydrolysis might become effective, forming the very slightly soluble hydrated manganese dioxide, and with this removed from the equilibrium system by precipitation, the reaction might proceed until concentrations were diminished to equilibrium conditions.

It is of interest to note that the precipitation began long before the solutions were entirely neutralized as shown by indicator tests. This was shown in another way by placing a crystal of iceland spar in the mixture of gold and manganous chlorides in solution. A slight effervescence occurred, and after a few hours the crystal was covered with a brown coat of manganese dioxide in which flakes of gold were plainly visible. The precipitation of gold was practically complete when an excess of MnCl_2 was employed, though this solution had at least the acidity of saturated carbonic acid.

An interesting reaction of similar nature was found to take place between auric chloride solution and manganous carbonate. The precipitated carbonate (doubtless amorphous, in part, at least) reacts at once and is turned to the dark brown hydrated dioxide. The crystallized carbonate, that is, the mineral rhodochrosite, reacts slowly, but, after a day,

¹ Paper presented at the Milwaukee meeting of the American Chemical Society, March, 1913.

a crystal was coated with dark brown and flakes of gold were plainly discernible.

SUMMARY

If we suppose manganese tetrachloride to be an intermediate product, present only in very minute traces, we may find in it some basis of explanation. Suppose

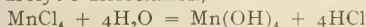


Since tetravalent manganese is an exceedingly weak base it should be little ionized, but it may be subject to two other sorts of dissociations, namely:

1. A molecular dissociation,



2. Hydrolytic dissociation,



Theoretically we should have the hydrolysis constant

$$\frac{\text{Mn}(\text{OH})_4 \times (\text{HCl})^4}{\text{MnCl}_4} = K$$

assuming hydrolysis according to the above equation. It is obvious that the presence of acid would tend to cut down the hydrolysis and allow the tetrachloride to become sufficiently concentrated to make its molecular dissociation appreciable—the greater the concentration of acid the greater this tendency—and we may, in this way, easily obtain conditions under which free chlorine is liberated, as in the chlorination process.

If, however, the acid concentration is reduced below a certain figure the concentration of the tetrahydroxide will reach saturation. Any further reduction of acidity must result in the precipitation of the hydrated dioxide. It will be seen that such an adjustment may be very delicate indeed—and this seems to be supported by the lack of success in preparing the tetrachloride, subject, as it would be, to both hydrolytic and molecular dissociation.

DEPARTMENT OF GEOLOGY
UNIVERSITY OF CHICAGO

SOLUBLE ARSENIC IN MIXTURES OF LEAD ARSENATE AND SOAP¹

By H. V. TARTAR AND L. A. BUNDY

Received April 7, 1913

There has been some complaint from horticulturists that some difficulty was experienced in keeping arsenate of lead in suspension in water while spraying. It is claimed that the lead arsenate settles out too quickly and it is difficult to keep it stirred up. This seems to be especially true when knapsack sprayers are used. Parker² has suggested that a soap solution might be used to aid in keeping the arsenate of lead in suspension. Parker reported results of laboratory experiments which indicate that a soap solution keeps the arsenate of lead in suspension much better than water. He has also stated that the soap would be of value in causing the spray to spread more evenly over the surface of the leaves and, in midsummer spraying, the smooth skin of the apple.

Mr. W. H. Lawrence, Fruit Inspector of Hood River County, Oregon, advised the orchardists in

that locality to try the lead arsenate-soap mixture experimentally. The results of the experiments tried indicated that in some instances considerable injury was caused to the foliage of the trees. It was suggested that this foliage injury, which resulted apparently from the use of the spray, might be due to soluble arsenic compounds formed by the reaction of the soap with the lead arsenate. Consequently, some laboratory experiments were undertaken to ascertain the amount of soluble arsenic in mixtures of soap with the different lead arsenates. While there has never been any extensive use of the lead-arsenate soap mixture, the results obtained are of special interest in showing differences in the behavior of the arsenates.

Three samples of commercial lead arsenate were selected for the experiments. A brand which gave no test for acid arsenate (PbHAsO_4) when tried by Volck's test¹ was selected as a neutral (ortho) arsenate of lead [$\text{Pb}_3(\text{AsO}_4)_2$]. The other two brands were composed mostly of the acid arsenate of lead. The results of the analyses of the three brands were as follows:

	Sample Neutral arsenate Per cent	Sample Acid arsenate No. 1 Per cent	Sample Acid arsenate No. 2 Per cent
Moisture.....	49.51	47.82	47.39
Total arsenic oxide (As_2O_5).....	10.98	15.00	16.73
Soluble arsenic oxide.....	0.14	0.39	0.28
Total lead oxide (PbO).....	37.01	33.92	33.48
Water-soluble impurities other than arsenic oxide.....	1.01	0.88	0.72

Three kinds of soap were used: "Ivory," whale oil, and ordinary yellow laundry soap. The "Ivory" and the whale oil soaps did not contain any free alkali, while the yellow laundry soap contained a small amount.

The proportions of lead arsenate, soap and water which were used corresponded to those recommended for use in actual spraying practice. In each of the tests, 4.8 grams of lead arsenate, 4.8 grams of soap and 1 liter of water were used. Each sample of arsenate of lead was tried with each of the different soaps. In each instance, the soap was dissolved in about 500 cc. of water, the lead arsenate, after it had been worked up with a little water, was then added and the whole made to 1000 cc. volume. The mixtures were let stand for six hours with an occasional shaking and then filtered. The filtrates were then analyzed for their content of arsenic oxide. The determination of arsenic oxide was made by first digesting the solution with arsenic-free sulfuric acid and potassium sulfate until the solution was clear. The solution thus obtained was neutralized with sodium bicarbonate and titrated with standard iodine solution in the manner used in the modified Gooch and Browning method.² Great difficulty was encountered in filtering the solutions for the arsenic determinations. They filtered very slowly and it was found that a small amount of lead passed through into the filtrates.

¹ Paper presented at the Milwaukee meeting of the American Chemical Society, March, 1913.

² Montana Agr. Exp. Sta., Bull. 86.

¹ Science, New Series, 33, 866 (1911).

² Bureau of Chem., Bull. 107, Revised, p. 239.

It was difficult to ascertain if the lead was actually in solution or merely in suspension and to make the calculations for the amount of soluble arsenic on the safest basis, the lead was determined in the usual manner¹ and the amount of arsenic necessary to combine with the lead present was deducted from the total amount of arsenic found. The results obtained in this way are given in the following table:

SOLUBLE ARSENIC IN MIXTURES OF LEAD ARSENATE AND SOAP

Material used	Grams of soluble arsenic oxide (As ₂ O ₃)	Grams of arsenic oxide in lead arsenate used	Per cent of the arsenic oxide made soluble
Neutral (ortho) arsenate + "Ivory" soap.....	trace	0.527	0.00
Neutral (ortho) arsenate + whale oil soap.....	0.004	0.527	0.76
Neutral (ortho) arsenate + laundry soap.....	trace	0.527	0.00
Acid arsenate No. 1 + "Ivory" soap.....	0.173	0.720	24.02
Acid arsenate No. 1 + whale oil soap.....	0.164	0.720	22.77
Acid arsenate No. 1 + laundry soap.....	0.184	0.720	25.55
Acid arsenate No. 2 + "Ivory" soap.....	0.367	0.803	45.70
Acid arsenate No. 2 + whale oil soap.....	0.280	0.803	34.86
Acid arsenate No. 2 + laundry soap.....	0.368	0.803	45.82

These results show that in the mixtures of the soaps with the acid arsenates large amounts of arsenic are rendered soluble. The results also indicate that when a neutral (ortho) arsenate of lead is used with soap only a very small amount of arsenic is made soluble. Evidently, the use of a mixture of soap with an acid arsenate of lead for spraying purposes would be a dangerous practice, for the amount of soluble arsenic would be sufficient to badly burn the foliage of fruit trees.

CHEMICAL LABORATORY
AGRICULTURAL EXPERIMENT STATION
CORVALLIS, OREGON

MINERALOGICAL SOIL ANALYSIS

By Wm. J. McCaughey
Received March 25, 1913

The problem of soil fertility and sustained crop production is a difficult one and, as Cameron² has pointed out, is a function of many variable factors, all of which are dependent upon each other. The importance of the chemical composition of a soil was recognized by Liebig and since then many analyses of soils have been made for the purpose of indicating the soil fertility. To explain anomalous cases it became necessary to assume that these elements exist in the soil in combinations which are available or non-available to growing plants, and many methods of analysis were proposed and used in determining the amount of these elements available. Such methods, however, are arbitrary and add little to our knowledge of the actual composition of a soil.

The greater part of a soil consists of the residuum from rock disintegration and is composed largely of the minerals constituting the original rock and secondary mineral development due to the alteration of the original minerals of the rock mass. This is more or less modified by geological agencies which bring about the transportation of some of the minerals and the admixture of still other material. It has

been the experience of practical soil men that too little is known of the actual composition of soils. A soil examination consists usually in the mechanical analysis which tells only the composition in terms of the size of the soil grains regardless of their nature, and in the determination of the so-called plant foods which are soluble in constant boiling point hydrochloric acid.

Very little work has been done upon the mineralogical composition of soils, though it is obvious that differences in mineral composition will affect their physical and chemical properties. Mitscherlich has indicated that not only the size of the particles has a great influence upon the physical properties of a soil but also the shape of the particles, that is, the amount and *kind* of surface exposed. The recent development in the application of petrographic methods to the study of minerals in fine powder has furnished a valuable and fruitful method for soil work. The microscopic study of minerals has been developed around and practically confined to the study of igneous and metamorphic rocks. Little work has been found in the geological literature to indicate that such examinations have been made on soils. The most important of such examinations have been made by Sorby,¹ Retgers,² Schroeder Van der Kolk³ and Delage and Lagatu.⁴

The chemical and mineralogical study of soil formation and of rock weathering has received more attention from geologists than pure soil work. Mineralogical compositions of wind-blown dusts have been published from time to time. The first attempt to systematically apply petrographic methods for the mineralogical examination of soils was made in 1889 by Steinriede. Since then little work has been done along these lines except by Delage and Lagatu.

The mineralogical composition of a soil bears somewhat the same relation to the chemical analysis of a soil as the petrographic examination of a rock does to its chemical analysis. They each supplement each other. The chemical analysis does not reveal the nature of the chemical elements as they are found in the soil. The mineralogical examination on the other hand is concerned chiefly with the determination of the chemical compounds in which the elements are combined. Should more definite knowledge of the reaction of these minerals toward water be known, a mineralogical examination would be of greater value in determining the chemical properties of a soil. An approximation to the availability of these elements could then be known from their mineralogical combinations. Fortunately from the observation of the chemical alteration of these minerals in the soil a mineralogical examination offers, at least, a comparative estimate of the availability of

¹ "Microscopical Examination and Determination of Minerals in Sands and Clays," *Quart. J. Geol. Soc.*, **1880**, 50.

² "Mineral and Chemical Investigation of the Dune Sands of Holland," *Neues Jahrb. fur. Min.*, **1**, 16-74 (1895).

³ "Mineral Composition of Holland Sands," *Der Wandlungen der k. Akad. von Wetenschappen*, **1895**, et seq.

⁴ "Constitution of Montpellier Soils," *Ann. de l'ecole Nationale de Montpellier*, **4**, 200-2 (1905).

¹ Bureau of Chem., *Bull.* **107**, Revised, p. 239.

² "The Soil Solution," Easton, Pa. (1911).

these chemical elements in the different minerals.

The presence, in the soil, of certain minerals offers a clue to the identification of the rocks from which the soils were derived. Rocks are often not only characterized by the presence of certain minerals but often by peculiar characteristics in the minerals themselves, as to inclusions, elongation, undulatory extinction, etc., which are preserved in the soil grains themselves. In other words, the physical appearances and characteristics of the minerals are often distinctive enough to indicate their source, as the localities of megascopic specimens are often indicated by peculiarities in habit. Another advantage offered by the mineralogical examination of soils lies in the readiness with which such examinations can be made, the approximation of the chemical composition of soil and, in the latter case, the cheapness of this method of examination where a high degree of accuracy is not necessary. The mineralogical analysis should be of considerable value in the geological mapping of soils as to their origin, etc. In the mineralogical examination of a soil, admixture of soil material is indicated by the differences in the degree of chemical alteration of certain of the minerals, namely, orthoclase and biotite, or by differences in the contour of the mineral grains, notably quartz.

The four common potash-containing minerals found in soils in their order of potash content are: orthoclase, 16.9; microcline, 16.9; muscovite, 10.0; biotite, 9.0. Of these biotite is the one most readily decomposed under soil conditions, due probably to the effect of the iron oxide contained in the molecule. It is perhaps the potash mineral in which the potash is most available. The common potash mineral present in soils is orthoclase, and it is generally present in considerable amounts (3 to 30 per cent). It suffers decomposition less readily than biotite and is perhaps after biotite the mineral which furnishes the potash more readily, in maintaining the concentration of the soil solution.

Muscovite, the potash mica, is quite resistant to chemical disintegration and generally occurs in soils in unaltered fragments which would seem to indicate that this mineral does not materially contribute to the soil solution at least during the presence of biotite and orthoclase. This fact is more or less consistent with the experiments of Johnstone, who found that after one year's treatment with water carrying carbon dioxide, muscovite remained unaltered. Microcline, the triclinic potash feldspar, is very resistant to chemical decomposition and is found in the leached sands of the Coastal plain with the insoluble minerals—quartz, tourmaline, zircon, rutile, etc. It is questionable indeed if this mineral is of great value in the keeping up of the "normal" concentration of potash in the soil solution.

Apatite found in soils has invariably proven to be the fluorapatite and generally is found in slightly rounded prisms with very low birefringence. It is also found in tiny needles as inclusions in quartz and other minerals. At this time attention might be

directed to an error in judgment which might be quite easily committed in mistaking epidote on the basal pinacoid for prismatic apatite. These both have low birefringence, parallel extinction, and negative elongation. The epidote may be quite readily distinguished by tapping the cover glass until the mineral rotates about its axis of elongation. If the mineral is epidote, the birefringence will be much higher in this new orientation and the elongation positive. No change takes place in the case of apatite. Complete chemical analysis often shows phosphoric acid which is not available for the maintenance of the concentration of phosphoric acid in the soil solution since these grains are totally imbedded in quartz. There is probably a difference in the rate of solution of chlor and fluorapatites since the latter is the one found in soils. Chlorapatite when found does not show the clear cut appearance of the fluorapatite. These two are distinguished by differences in refractive indices.

Of the calcium minerals, epidote, hornblende, plagioclase and garnet seem to be the commoner ones. Of these minerals, the feldspars are the more available for the maintenance of the "normal" concentration of the soil solution. Hornblende seems to be the next available calcium mineral and then garnet and then epidote. Epidote is a normal constituent of most soils and is present in large, thick grains. Garnet being formed generally by contact metamorphism, is more or less restricted in its occurrence. Hornblende is the common calcium mineral and weathers generally forming chlorite, a magnesium aluminum silicate. In general in soils from the humid regions, even in those derived from limestone the absence of calcite is noteworthy.

In soils derived from limestone, small quartz crystals are so frequently found and so exceptional in other soils that their presence in soils would seem to indicate origin from limestone. The absence of pyroxene as a soil-forming mineral is noteworthy.

Especial attention should be directed to the phytolitharian sponge spicules, diatoms, rhizopoda casts found in some soils. These plant or animal remains indicate, by their presence, low submergence and swamp conditions which have been responsible for the mineralogical depletion of certain soil types. These organisms are of geological importance in the indication of conditions through which the soil has passed. Each of these organisms demand a particular environment for their growth, and their presence in a soil in large numbers indicates this particular condition at least during their time of flourishing. In this matter see Ehrenburg's "Mikrogeologie."

It may be said that as a general proposition the mineralogical composition of the silts in minerals other than quartz is much higher than in the sand separates, though as a rule, and especially is this so in loam and clay soils, the silt grains are not nearly as well preserved as in the sand separates. It would seem that the smaller the grain the greater the decomposition. It is reasonable to assume that the concentration of the soil solution will vary with the

mineral composition, as each of the minerals probably possesses a distinctive reaction toward water. The concentration of the soil solution will be determined, in general, by the minerals possessing the greater velocity of solution or decomposition. The minerals which furnish the plant food in the soil have their origin in igneous rocks or metamorphic rocks, and it is hardly likely that the reactions occurring in the soil by which the elements pass into solution are reversible; therefore, it is not likely that the soil solution will be of constant composition. These easily soluble or decomposable minerals will furnish the necessary elements to maintain the concentration of the soil solution. There would then be a tendency toward the survival of the more insoluble or the difficultly decomposable minerals which in time would be called upon to furnish the necessary "plant food."

Another factor of importance in considering variation in concentration of the soil solution, is the recovery rate, that is, the time required to attain the normal concentration in the soil solution after rainfall. The rate of recovery will depend not only on the nature of the minerals composing the soil but also upon the percentage composition of the more soluble or easily decomposable minerals. In soils composed of the same minerals that soil which has the greater proportion of the more soluble or easily decomposable minerals will have the quicker recovery to the normal concentration after rainfall. In other words availability as applied to unfertilized soils may be expressed by the mineral composition of the soil and the rate of recovery expressed by the percentage composition in easily soluble or decomposable minerals.

OHIO STATE UNIVERSITY
COLUMBUS

ON THE INFLUENCE OF THE LIME-MAGNESIA RATIO

By P. L. GILE AND C. N. AGETON

Received April 29, 1913

In a recent number of *THIS JOURNAL* (Vol. 5, No. 1, p. 33) attention was called to the fact that certain Porto Rican soils which are exceptionally productive for citrus trees, pineapples and sugar cane, have exceedingly wide ratios of lime to magnesia. It was pointed out that if Loew's hypothesis of the lime-magnesia ratio holds true for soil conditions, and if this ratio really is a controlling factor in fertility, then those soils with exceptionally wide ratios certainly should not be more than ordinarily productive, and if they are very productive it is evidence of the untenability of Loew's hypothesis.

Loew in commenting on these facts¹ holds that they do not constitute evidence against his theory, since citrus fruit and pineapples "are but other examples of apparent exceptions in regard to the lime-factor. Such exceptions are the lime-loving plants, e. g., the grapevine, as the writer has pointed out repeatedly. These plants are capable of precipitating, as oxalate, the excess of lime carried into the plant by the transpiration process." He further states: "Thus a properly working ratio of lime to magnesia is secured in the cells when the plants grow on soils

rich in lime * * * * Hence the view, that the favorable development of these plants on soils very rich in lime and poor in magnesia would be a proof against the influence of a certain ratio of lime to magnesia in soils upon other plants which do not produce oxalates, is not tenable."

It is certainly not our opinion that what holds true for one species of plant necessarily holds true for all plants. But according to our understanding of the hypothesis as Loew has enunciated it, all higher plants are affected by the lime-factor, although lime-loving plants have a higher optimum ratio than others.²

Now, pineapples cannot be excepted from the influence of the lime-factor (if such influence exists) on the ground that they are lime-loving plants, for field observations and direct experiments have shown that pineapples are, on the contrary, strongly calcifuge or "kalkfeindlich." The intolerance of pineapples for calcareous soils was pointed out in 1911 by one of us in *Bulletin* 11 of this Station. In this bulletin are detailed observations in Porto Rico and other countries, also direct experiments which show that pineapples cannot endure much carbonate of lime in the soil unless a large amount of organic matter is also present.³

While citrus trees are not calcifuge, observations in Porto Rico at least would not lead one to classify them as lime-loving. To the knowledge of the writers there have been no direct experiments nor studies showing the tolerance of citrus trees for large amounts of lime in the soil. It is certain, however, that citrus trees in California planted on land with marly subsoils are affected with nutritional disturbances,⁴ which would hardly lead one to believe that they are especially lime-loving.

In regard to the formation of oxalates, pineapples cannot be considered peculiar, since the occurrence of oxalates in plant cells is now known to be very common. Kohl states: "Dasselbe [Calciumoxalat] ist in allen Pflanzenorganen und Geweben gefunden worden."⁵ In regard to its distribution in plants in general, Coulter, Barnes and Cowles state: "Calcium oxalate is found in every large group of plants except bryophytes."⁶ Euler states: "Tritt die Oxalsäure sowohl in niederen als besonders in höheren Pflanzen sehr häufig auf."⁷ Even in the grasses where

¹ Loew, *Landw. Jahrb.*, 1902, 563, states: "Freilich können viele Pflanzen durch Niederschlagung eines Teiles des aufgenommenen Kalks als Calciumoxalat den Ueberschuss des gelösten Kalks unwirksam machen und dadurch des normale Funktionieren im Gange halten. Aber dieser durch Anpassung erworbene Fähigkeit ist eben auch nur eine begrenzte." From this statement one would certainly suppose that the limit of toleration of plants forming oxalates for an unfavorable lime factor would be transcended at a lower ratio than 24/1 to 500/1.

² By consulting the data in this bulletin it can be seen that pineapples cannot be called "lime-loving," on account of their growth on soils rich in carbonate of lime (the sense in which this term is usually used), nor on account of the amount of lime which is present in the ash of the plant. Also pineapples thrive on soils which are very poor in lime; see Miller and Hume, Florida Station, *Bull.* 68.

³ Hilgard, California Sta., *Circ.* 27.

⁴ F. G. Kohl, "Anatomisch-physiologische Untersuchung der Kalksalze und Kieselsäure in der Pflanze" (1889), cited from *Jahresb. u. d. Agriechemie*, 1889, 121.

⁵ Coulter, Barnes and Cowles, "A Textbook of Botany," 1910; also see Czapek, "Biochemie der Pflanzen," 1908, Vol. II, pp. 417-420.

⁶ H. Euler, "Grund. u. Ergeb. d. Pflanzenchemie," 1908, Vol. I, p. 16.

¹ *THIS JOURNAL*, 5, No. 3, 257.

oxalates were supposed to occur very seldom, Montverde has found crystals of calcium oxalate quite widely distributed: of 550 species from 94 families, oxalates were found in 162 species from 92 families.¹ In maize, which Loew states grows best at the lime factor of 2 : 1, Benecke has found calcium oxalate.²

The evidence we have offered concerning the untenability of Loew's hypothesis for ordinary soil conditions can hardly be disregarded, then, on the grounds assumed by Loew, since pineapples and citrus trees are not lime-loving plants, nor is the property of forming oxalates peculiar to a few plants.

We also pointed out that a soil where the ratio of lime to magnesia varied from 24/1 to 1461/1 gave an average yield of 60 tons of sugar cane (variety Christalina) last year. The yield obtained is exceptional for Porto Rico and very good for any country. The fact that this soil with an exceptionally wide ratio of lime to magnesia is more than ordinarily productive we take to be further proof that Loew's hypothesis does not hold for ordinary soil conditions.

Loew objects that tankage or cottonseed meal might have been used on this soil as a fertilizer in which case the sugar cane would become almost independent of the lime-factor in the soil, because of the lime and magnesia contained in the fertilizer "in an easily available form." This field in some years has been fertilized with a complete fertilizer at the rate of about 500 lbs. per acre, and we are under the impression that tankage, cottonseed meal and certainly barnyard manure have never been used here. If, however, 500 lbs. of tankage per acre had been applied to the soil in question we fail to see how this application could materially influence the effect of the lime-magnesia ratio if the ratio has any such potent action as Loew in previous articles has attributed to it.

The analyses (given in the previous article) show this soil to contain from 1,044,400 to 1,287,600 lbs. of CaO in the form of carbonate in an acre foot and from 800 to 62,400 lbs. of MgO.³ From experiments in Japan, Loew concludes that magnesium sulfate is about ten times as effective as the natural magnesium carbonate in counteracting an excess of lime.⁴ On this basis, something like 1,000,000 lbs. of magnesium carbonate or 100,000 lbs. of magnesium sulfate per acre would be required to effect the proper ratio. How, then, can the magnesium contained in an ordinary application of tankage or cottonseed meal balance an excess of a million pounds of lime per acre? If it can balance this excess, of what significance is the determination of the original lime-magnesia ratio in the soil?

According to the hypothesis of the lime-magnesia ratio, the injury to plant growth arising from excessive ratios of lime to magnesia in the soil is caused by an undue preponderance of lime in the plant cell. By the law of mass action the lime, displacing the magnesium, combines with the phosphoric acid in the cell, preventing the assimilation of phosphoric acid and the

plant suffers from phosphorus starvation. Some plants, however, are partially independent of unfavorable ratios in the soil, since they have the power of precipitating an excess of lime as oxalate and so the balance between the "physiologically active" lime and magnesia in the plant cell is maintained. This hypothesis assumes, then, that the amount of lime and magnesia absorbed by the plant is affected more or less by the ratio in which these bases exist in the soil, otherwise how could the injury take place in the plant cell?

Certain results which we have secured in the study of another problem are interesting in connection with this hypothesis. In the course of this work the growth of bush beans (variety Improved Golden Wax) was compared on a soil containing varying amounts of calcium carbonate. The plants were grown in plots which were 10 × 20 ft. in area and 2 ft. deep. The plots were equally and liberally fertilized from time to time so that the plants received sufficient nitrogen, potash and phosphoric acid in all the plots, acid phosphate, sodium nitrate and high-grade sulfate, or muriate of potash being used. There were four plots: Plot I contained the soil with no addition of carbonate of lime, Plot II approximately 4 per cent CaCO₃, Plot III 15 per cent CaCO₃, and Plot IV 30 per cent CaCO₃. The plants were here grown under perfectly normal conditions of root space, moisture conditions, etc.

Table I gives the amount of lime and magnesia in the fine earth soluble in hydrochloric acid of sp. gr. 1.115,⁵ also the carbonate content in the four plots.

TABLE I				
Plot no.	I	II	III	IV
Per cent	Per cent	Per cent	Per cent	Per cent
CaO . . .	1.03	4.06	10.90	21.24
MgO . . .	1.37	1.65	0.79	1.51
CO ₂	0.00	2.18	7.84	15.35

The ratios of lime to magnesia in Plots I to IV were, then, 0.8, 2.5, 13.8 and 14.1 to 1. Loew gives 3 : 1 as the lime factor most favorable for leguminous plants so we should expect the best growth of plants in Plot II and a depression of growth in Plots I, III and IV, if the lime-factor exerts much influence on the growth.

Six crops of beans, namely, Series A, B, C, D, E, and F were grown at different times in the course of three years. In Series A the beans were allowed to mature and their weight obtained. The plants in Series B, C, D, E and F were harvested when the plants were in bloom and had attained their maximum growth without any of the leaves being withered. Samples of these crops were preserved for an ash analysis. In Table II are given the absolute weight of the different crops from the four plots and also the relative yields, calling the yield of Plot I equivalent to 100.

It can be seen that bush beans seemed to do slightly better with increasing amounts of carbonate of lime in the soil, and that the growth on the soil with the lime factor 14 was equal to, or a little better than that made on the soil with the lime-factor 2.5. According

⁵ This is practically the method prescribed by Loew for determining the lime-magnesia ratio in the soil. *Landw. Jahrb.*, 1906, 537.

¹ N. A. Montverde, *Botanisches Centralblatt*, 43, 327.

² W. Benecke, *Botanische Zeitung*, 61, 79 (1903).

³ Using 4,000,000 lbs. as the weight of an acre foot of soil

⁴ Loew, *Landw. Jahrb.*, 42, No. 1, 190.

TABLE II—GROWTH OF BUSH BEANS ON SOIL WITH DIFFERENT AMOUNTS OF LIME

Number of plot	I	II	III	IV
Ratio CaO/MgO in soil	0.8	2.8	13.8	14.1
Weight, seeds from 80 plants, in grams, Series A	125	123		157
Weight, 60 whole plants, in grams, Series B	2086	1913	2112	2885
Weight, 61 whole plants, in grams, Series C	488	810	887	660
Weight, 61 whole plants, in grams, Series D	753	1038	983	984
Weight, 64 whole plants, in grams, Series E	670	740	690	615
Weight, 32 whole plants, in grams, Series F	777	776	695	637
Total weight in grams of Series B to F	4741	4974	5007	5721
Relative yields calling that of Plot I = 100, Series A	100	97		124
Relative yields calling that of Plot I = 100, Series B	100	92	101	137
Relative yields calling that of Plot I = 100, Series C	100	112	123	145
Relative yields calling that of Plot I = 100, Series D	100	138	127	127
Relative yields calling that of Plot I = 100, Series E	100	110	103	92
Relative yields calling that of Plot I = 100, Series F	100	100	96	82
Average of relative yields, Series B to F	100	110±3.4	109±4.8	117±8

to the hypothesis of the lime-magnesia ratio, the bush beans grown on the soils with the high percentages of lime and unfavorable lime-factors should contain more lime than the plants grown on the soils with less lime and more favorable lime-factors, although if the growth is unaffected, the plants grown on the soils with the high lime-factors might remove part of the absorbed lime from participating in the physiological processes of the plant by precipitation as oxalate.

TABLE III—ANALYSES OF BUSH BEANS (WHOLE PLANT), GROWN ON SOILS WITH DIFFERENT AMOUNTS OF LIME

Series analyzed	Analysis of carbon-free ash								Ash constituents in dry substance of plant							
	Series B				Series D and F				Series B				Series D and F			
Plants from plot	I	II	III	IV	I	II	III	IV	I	II	III	IV	I	II	III	IV
Ratio CaO/MgO in soil	0.8	2.5	13.8	14.1	0.8	2.5	13.8	14.1	0.8	2.5	13.8	14.1	0.8	2.5	13.8	14.1
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Carbon-free ash	35.54	29.95	26.02	28.53	25.91	26.82	28.12	25.57	10.62	11.48	11.63	12.05	11.20	11.20	10.82	11.73
CaO	12.31	12.31	11.15	10.03	7.67	7.90	7.28	6.30	3.78	3.44	3.02	3.44	2.90	3.01	3.04	3.00
MgO	8.14	7.39	7.16	7.02	8.27	8.36	8.67	7.94	1.15	1.41	1.30	1.21	0.86	0.89	0.79	0.74
P ₂ O ₅	32.98	32.38	31.82	34.45	33.82	31.85	36.82	35.19	0.86	0.85	0.83	0.84	0.93	0.94	0.94	0.93
K ₂ O	1.54	1.44	1.22	0.99	1.28	0.96	0.88	0.82	3.51	3.72	3.70	4.14	3.78	3.58	4.00	4.13
Fe ₂ O ₃	12.05	12.85	10.80	8.63	10.11	10.08	8.97	8.38	0.16	0.16	0.14	0.12	0.14	0.11	0.10	0.10
SiO ₂									1.28	1.47	1.26	1.04	1.13	1.13	0.97	0.98
N									4.03	3.62	3.58	3.76	3.77	3.85	3.62	3.76

In other words, the plants grown on all four soils might contain the same amount of "active or physiological" lime, but those grown in Plots III and IV where the lime factor is 14 should contain in addition considerable calcium precipitated as oxalate. It will be seen that the following analyses do not bear out such an assumption.

In Table III are given the analyses of the beans (cut in bloom) from the four soils, using the whole plant for analysis except the roots. Crop B was analyzed alone, Crops D and F were analyzed together, using a composite sample composed of equal parts of crops D and F. The percentages of the different elements in the ash and the percentages in the oven-dry substance of the plant are given.

The degree to which the varying amounts of lime in the soil has affected the ash composition and quantity of the elements in the dry substance of the plant is better shown in Table IV. Here the amounts of the different elements present in the plants grown in Plot I are given as 100 and the amounts present in the plants grown on Plots II, III and IV are expressed relative to 100. To save space the average, only, of crops B, D and F are given. In calculating the average twice the value was given to the analysis of crops D and F that was given to the analysis of crop B, so the average gives an equal value to each crop grown.

TABLE IV—RELATIVE ASH COMPOSITION OF PLANTS FROM DIFFERENT PLOTS

Plants from plot	Relative composition of ash of plants from different plots. Plot I = 100				Relative amount of elements in dry substance of plants from different plots. Plot I = 100			
	I	II	III	IV	I	II	III	IV
Ratio CaO/MgO in soil	0.8	2.5	13.8	14.1	0.8	2.5	13.8	14.1
Carbon-free ash	100	97	97	93	100	103	101	108
CaO	100	107	98	86	100	109	99	93
MgO	100	98	99	93	100	100	100	99
P ₂ O ₅	100	94	104	104	100	99	106	112
K ₂ O	100	81	73	64	100	86	77	72
Fe ₂ O ₃	100	102	89	79	100	105	90	85
SiO ₂	100	102	89	79	100	105	90	85
N	100	94	98	98	100	94	98	98

It can be seen from Table IV that the percentage of lime in the ash and in the dry substance of the plant is practically constant, irrespective of the amount of lime in the soil where the plants were grown. The same is true of the magnesia, except the results are not quite so uniform.

The degree to which the lime-magnesia ratio in the

plant corresponds to the lime-magnesia ratio in the soil is shown in Table V.

Plot No.	I	II	III	IV
Ratio CaO/MgO in soil	0.8	2.5	13.8	14.1
Ratio CaO/MgO in the plant	3.35	3.08	3.36	3.66

Thus the lime-magnesia ratio in this plant bore no relation to the lime-magnesia ratio in the soil.

Now, bush beans appear to be independent of the lime-magnesia ratio in these soils and also of the increasing amounts of carbonate of lime. This result, of course, does not apply to all plants but it stands for one plant at least, and probably a certain number of plants. Since the lime content of the plants remained constant with increasing amounts of lime in the soil

it does not seem possible that this plant could have adapted itself to the conditions by precipitation of lime as oxalate. It does seem that the independence of the plant to these soil conditions is due to the regulatory power of the root cells in the absorption of nutrients.

While we believe that ratios of different salts, including lime and magnesia, affect plant growth under certain conditions, it does not seem, with our imperfect means of determining the soil nutrients available to or affecting the plant, that the hypothesis of the lime-magnesia ratio should be considered as applying to all soil conditions. Moreover, work on balanced solutions and the regulatory power of plant cells in the absorption of nutrients would seem to indicate that the whole subject is more complicated than was supposed when Loew formulated his hypothesis.

PORTO RICO AGRICULTURAL EXPERIMENT STATION
MAYAGUEZ

A SIMPLE METHOD FOR PREPARING NEUTRAL AMMONIUM CITRATE SOLUTION

By A. J. PATTEN AND W. C. MARTI

Received April 9, 1913

The necessity of having a strictly neutral solution of ammonium citrate for the determination of available phosphoric acid in fertilizers is recognized by every fertilizer chemist. Methods for preparing such a solution have been discussed by the Association of Official Agricultural Chemists and investigated by many of its referees on phosphoric acid. This subject has also been studied by the Division of Fertilizer Chemists of the American Chemical Society, but to-day there are almost as many methods in use as there are laboratories doing fertilizer work.

Some chemists are still using the corallin method, some the alcoholic calcium chlorid method, some the azolitmin method proposed by Hand¹ and still others use a slight excess of ammonium hydroxid and depend upon the volatilization of the ammonia, upon long standing, to make the solution neutral.

McCandless,² when referee on phosphoric acid for the Association of Official Agricultural Chemists in 1908, compared solutions of ammonium citrate made by different chemists. In nine different solutions the ratio of ammonia to anhydrous citric acid was found, by analysis, to vary from 1 : 3.775 to 1 : 4.189. Doctor McCandless commented upon the unreliability of the methods then in use and closed his report with the following words: "While the referee has a strong conviction that the only proper method of making the solution is by analysis and calculation of the exact quantity of ammonia or citric acid to be added to it, still he hesitates to urge it officially, as no work has yet been done by any other referee along this line, and because the referee is himself no longer an official chemist."

Somewhat later the Fertilizer Division of the American Chemical Society proposed that the ratio of ammonia to citric acid should be 1 : 4.25. Such a solution, however, would be distinctly acid and would give higher results for available phosphoric acid than

a solution having the ratio of the tri-ammonium salt.

More recently a method based upon the change in electrical conductivity of a solution as it changes from an acid to an alkaline reaction was proposed by Hall and Bell³ and later by Patten and Robinson.⁴ This method gives satisfactory results and is not difficult of operation, but owing to the expensive apparatus required or for other reasons it has not been generally adopted. Later Bell and Cowell⁵ proposed two methods for preparing neutral ammonium citrate solutions but they present difficulties of manipulation that will undoubtedly militate against their general acceptance. There is still, therefore, the need of a method that will be simple, easy of manipulation, rapid and accurate and that does not call for unusual or expensive apparatus.

The method to be proposed fulfills these requirements and is based upon the work of Schiff⁶ who found that ammonia unites with formaldehyde to form hexamethylenetetramin according to the following equation:



Schiff also found that the same reaction takes place between salts of ammonia and formaldehyde and that the acid may then be titrated with a standard solution of sodium or potassium hydroxid, using phenolphthalein as indicator. Herstein⁷ made use of this reaction as a means of testing the purity of ammonium salts, and states that it gives satisfactory results with ammonium chlorid, bromid, iodid, fluorid, sulfate, acetate, oxalate, citrate, thiocyanate and molybdate.

The method as adopted by us is called the "titration method" and is essentially as follows: Fifty cc. of a citrate solution are carefully measured into a 250 cc. flask, made up to the mark with water and thoroughly shaken. Five cc. of the diluted solution are then measured (preferably by means of a burette) into a beaker, 4 cc. of a perfectly neutral 40 per cent solution of formaldehyde added and titrated with $N/10$ NaOH, using phenolphthalein as indicator. The pink color should remain after the solution is brought to boiling. The ammonia is determined in 5 cc. of the diluted solution in the usual manner by distilling with magnesia. The difference between the acid and ammonia titration gives the number of cubic centimeters of $N/10$ NH_3 required to neutralize 1 cc. of the acid citrate solution, from which the amount of a stronger solution of NH_4OH required to neutralize any given amount of the acid solution may be easily calculated.

The titration method was first tried out by us on a solution of ammonium citrate made neutral by the conductivity method and the ratio of ammonia to anhydrous citric acid was found to be 1 : 3.765, the same as for triammonium citrate. We then compared the titration method with the conductivity method for preparing neutral solutions. For this purpose a stock solution of citric acid was nearly neutralized

¹ *J. Am. Chem. Soc.*, **33**, 711 (1911).

² *This Journal*, **4**, 413 (1912).

³ *J. Am. Chem. Soc.*, **35**, 49 (1913).

⁴ *Lieber's Annalen*, **319**, 76 (1901).

⁵ *Bur. of Chem., U. S. Dept. Agr., Bull.* **150**, 47.

⁶ *Bur. of Chem., U. S. Dept. of Agr., Bull.* **132**, 11.

⁷ *Ibid.*, **122**, 147.

with ammonium hydroxid, being careful to keep the specific gravity above 1.09. By the conductivity method it was found that 25.9 cc. of a 5 per cent solution of ammonium hydroxid were required to neutralize 1000 cc. of the solution and by the titration method 25.95 cc. were required. With another citrate solution 35.4 cc. of a 5 per cent solution of ammonium hydroxid were required per liter by the conductivity method and 35.6 cc. by the titration method.

We next determined by the titration method the amount of citric acid and ammonia contained in one liter of a strictly neutral solution of ammonium citrate, of exactly 1.09 specific gravity, with the following results:

- 1 cc. citrate sol. gave 26.34 cc. $N/10$ NH_3
- 1 cc. citrate sol. gave 26.33 cc. $N/10$ $C_6H_8O_7$,
equivalent to 44.76 grams NH_3 per liter
equivalent to 168.57 grams $C_6H_8O_7$ per liter
Ratio of NH_3 to $C_6H_8O_7$ = 1 : 3.766.

The three solutions claimed to be neutral by McCandless contained 44.3 grams NH_3 and 168.76 grams $C_6H_8O_7$ per liter, the ratio being 1 : 3.809. The results obtained by us conclusively prove that such a solution would be slightly acid, which fact is further substantiated by the ratio of ammonia to anhydrous citric acid being too wide.

SUMMARY

The titration method of preparing neutral ammonium citrate solutions is accurate and easy of manipulation.

It establishes beyond a doubt that the ratio of ammonia to anhydrous citric acid in the neutral solution should be 1 : 3.765 and that one liter of 1.09 specific gravity should contain 44.76 grams NH_3 and 168.57 grams $C_6H_8O_7$.

The titration method affords a simple means of comparing ammonium citrate solutions made in different laboratories.

MICHIGAN EXPERIMENT STATION
EAST LANSING

THE FLUIDITY OF BUTTER FAT AND ITS SUBSTITUTES

By GEORGE F. WHITE AND RALPH H. TWINING

Received April 7, 1913

The study of the viscosities of butter fat and oleomargarine as a problem of more or less interest, has already been taken up by several investigators with different methods of approach and different types of viscosimeters. Wender¹ worked with an instrument of the Ostwald class, modified so that, according to his statement, it could be cleaned with greater speed and ease. The Reichert-Meissl number of each sample was taken as a measure of purity. The fats were dissolved in chloroform, the viscosity of the solvent being taken into consideration. Wender found that the viscosity of oleomargarine was always greater than that of butter and with both decreased with rise in temperature, but did not change on standing for a considerable length of time. Further, although the viscosities of the butter fats were fairly constant, there were appreciable differences in the margarines from different sources. The amount of mar-

garine added could be approximately determined.

Killing² contributed nothing new in his study of the viscosities of butter and other fats, and his apparatus was so crude that no advance was made.

Raffo and Foresti,³ in an article on a "New Method for the Determination of Margarine in Butter," describe results obtained by an Ostwald instrument. They used butter from two sources and took the viscosities at 50° C. of the fats obtained by melting and filtering from curd and water. The time of flow was found to increase as the percentage of oleo fat increased, different samples giving concordant results. Their data indicate roughly that the viscosity is some function of the composition, but what particular function is not stated.

It is evident that any connection between the viscosity and the composition of butter fats, if it exists, has not been clearly and definitely established. A study of this important relation should therefore reveal by the use of accurate methods of analysis, results of especial value and interest. It is our purpose in this article to present the results of a series of viscosity measurements of various butter and oleomargarine samples, and of mixtures of these of known composition. By utilizing a viscosimeter which enabled us to express viscosities in absolute units, a definite standard of comparison may be adopted. Such measurements are entirely independent of the apparatus employed, and the "times of flow," which are recorded in so many works of this nature and which mean nothing to anyone else than the observer and his particular viscosimeter, do not need to be considered.

We prepared our samples, obtained from various sources, by melting at the lowest possible temperature and allowing to stand for two or three hours in that condition. The curd and water settled to the bottom leaving the clear supernatant fat which was decanted through a filter. The following constants were taken: the iodine number which shows the amount of unsaturated acids present, the saponification number, the percentage of soluble and insoluble acids, the volatile acids, the densities at 40°, 65°, and 90° C., and the viscosities at intervals of 10° from 40° to 90° C. These constants, while by no means representing a complete analysis, give a very definite idea of the purity and the composition of the fat examined.

The iodine number was obtained by treating about one-half a gram of fat with 50 cc. of Hubl's solution (mercuric chloride and iodine in alcohol), and titrating the remaining iodine with sodium thiosulfate solution after three hours' standing to ensure complete absorption. The number is expressed in the percentage of iodine absorbed, *i. e.*, the number of grams of iodine taken up by 100 grams of fat.

The saponification was carried out with an alcoholic potassium hydroxide solution, the mixture being heated on the water bath with a reflux condenser for thirty minutes, and the excess alkali then titrated with half-normal hydrochloric acid. The saponification (Koettstorfer) number is expressed as milligrams

¹ *Z. angew. Chem.*, **1894**, 643; **1895**, 102. *J. Soc. Chem. Ind.*, **1895**, 198.

² *Gazz. chim. ital.*, **39**, 441 (1911).

³ *J. Am. Chem. Soc.*, **17**, 719 (1895).

of potassium hydroxide required to saponify 1 gram of fat. After the titration, 1 cc. exceeding the exact amount of half normal hydrochloric acid necessary to free the fatty acids was added. The insoluble acids, after cooling, were washed free from the soluble acids and the latter titrated with decinormal alkali, the result being calculated as per cent butyric acid. The cake of insoluble acids was dried and weighed and the per cent calculated.

To obtain the Reichert-Meissl number, which is perhaps the most important of these constants, about 5 grams of fat were saponified by heating under pressure with caustic soda and 95 per cent alcohol. Sulfuric acid in sufficient amount to free the fatty acids was added and the whole again heated under pressure. The flask was then connected with a condenser, the volatile acids distilled off, and an aliquot portion titrated with decinormal alkali after filtering. The result signifies the number of cubic centimeters of decinormal potassium hydroxide solution required to neutralize the volatile acids obtained from 5 grams of fat.

The densities of the samples were taken in an ordinary Ostwald pycnometer, comparison being made with the density of water at 4° C.

Of particular interest to us in our study of the viscosity of these very viscous liquids is the work of Scarpa,¹ who, discerning the sources of error in the viscosimeters of various types, devised one of very great accuracy and which was capable of wide application. In his instrument there was a capillary tube from 5 to 10 cm. long and about 0.2 mm. inside diameter. The lower end of the vertical capillary dipped into a test tube containing oil; the upper end was joined to a series of bulbs of varying volume. At the top it was connected to an apparatus for maintaining reduced pressure, and also with a manometer. The whole was put under diminished pressure and the liquid drawn up to fill one or more of the bulbs, the amount so drawn through the capillary depending on the viscosity. The time t_1 was observed. By use of one or more bulbs the times of flow of liquids of very different viscosities were not widely divergent. The liquid was next allowed to flow back under its own weight and atmospheric pressure, taking the time t_2 . The viscosity is proportional to the ratio $t_1 t_2 / (t_1 + t_2)$. The constant of proportionality is dependent neither upon the surface tension nor the quantity of the liquid. A characteristic value for the proportionality constant could be obtained by using the instrument under the same reduced pressure. By determining $t_1 t_2 / (t_1 + t_2)$ with the same quantity of liquid at the same temperature, relative results could be obtained. Values obtained by the Scarpa and Engler instruments were very widely divergent, the former being by far the more consistent, especially with very viscous oils.

While Scarpa's viscosimeter is evidently one of considerable efficiency, we believe that the instrument described by one of us,² and which has been applied to a study of various liquids,³ presents to a

greater degree the advantage of facility of manipulation combined with great accuracy. As do the viscosimeters of Thorpe and Rodger,⁴ and Bingham and White,⁵ it gives viscosity results in absolute units which are corrected for the gain in kinetic energy involved in the flow of the liquid through the capillary tube. By its symmetrical shape there is only a small correction to the pressure as measured in the manometer. Finally, by varying the pressure, fluid and viscous liquids may be measured in the same instrument and at all temperatures.

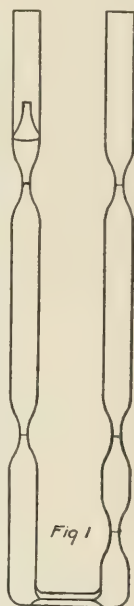
Since the viscosimeter has been described in detail in previous articles³ and has been modified in only one respect for this work, a very brief description will suffice. It consists (Fig. 1) of two vertical glass limbs as nearly alike as possible, except for there being a trap in one, these limbs being connected by a horizontal capillary tube fused into their lower ends. The capillary is of about 0.1 mm. internal diameter and of a length suited to the nature of the liquids to be investigated. On one limb two marks are so placed that, in falling from the higher to the lower, from 2 to 4 cc. of liquid passes through the capillary. This volume is determined before the viscosimeter is put together. Above the higher mark there is a trap. On the other limb, not far above the capillary, another mark is etched. The volume of liquid used is always the amount required to fill the instrument from this last mark to the top of the trap in the other limb.

The modification of the viscosimeters previously used, though only slight, has made the instrument easier to make and to calibrate. In this work, instead of calibrating two limbs, we have taken the time of falling from the higher to the lower mark, *VISCOMETER B* then reversing the pressure, taking the time of rising between the same marks. This has proved as satisfactory as the former method and saves the calibration of one limb.

The following formula was used in the calibration of the viscosity results:

$$\eta = \frac{\pi r^4 p t}{8 v l} - \frac{v d}{8 \pi l}$$

η is the viscosity, r the radius, l the length of the capillary, v the volume of liquid passing through the capillary, d the density of the liquid, p the pressure, and t the time of flow. The constants $\pi r^4 / 8 v l$ and $v / 8 \pi l$ were determined by taking the time of flow of water at 30° and a suitable pressure, the value of η being taken from the data of Thorpe and Rodger. The correction to the pressure for any asymmetry in the instrument has an opposite effect according to



¹ Gazz. chim. ital., **40**, II, 261 (1911).

² Biochem. Z., **37**, 482 (1911).

³ THIS JOURNAL, **4**, 106, 267, 878 (1912).

⁴ Phil. Trans. London, (A), **185**, 397 (1894).

⁵ Z. physik. Chem., **80**, 670 (1912).

⁶ Loc. cit.

whether the liquid is rising or falling in a certain (the calibrated) limb. If p_1 and t_1 , and p_2 and t_2 , represent the times of flow and the pressures when the liquid is rising and falling, respectively, or *vice versa*, the correction to the pressure x may be calculated according to the equation

$$x = \frac{p_1 t_1 - p_2 t_2}{t_1 - t_2}$$

may be suspected. Of course an adulterated butter may be made more fluid by the addition of one of many oils possible, and such admixtures could be detected only by a determination of other constants.

That the better grades of butter are the less viscous is evidenced by the constants of the four samples studied. Sample I has the least amount of soluble and volatile acids, and its high viscosity corresponds

TABLE I

Sample	Iodine number			Saponification number			Insoluble acids			Soluble acids			Reichert-Meissl No.
	I	II	Av.	I	II	Av.	I	II	Av.	I	II	Av.	
Butter I.....	36.95	37.13	37.04	228.9	229.1	229.0	89.41	89.60	89.51	3.421	3.481	3.451	25.16
Butter II.....	38.10	37.92	38.01	224.1	225.0	224.6	88.47	88.92	88.70	3.869	3.911	3.890	26.69
Butter III.....	30.90	31.02	30.96	231.3	231.5	231.4	89.23	89.14	89.18	4.017	4.017	4.017	27.04
Butter IV.....	34.07	34.26	34.17	230.4	230.1	230.3	88.71	89.10	88.91	4.026	4.026	4.026	27.08
Oleomargarine I.....	58.77	59.17	58.97	194.9	195.3	195.1	94.74	95.04	94.89	0.1	1.1	0.1	0.1660
Oleomargarine II.....	64.15	64.92	64.54	191.3	190.9	191.1	94.75	94.75	94.75	Less than	0.1	0.1	1.100
Oleomargarine III.....	67.92	67.92	67.92	136.3	136.9	136.6	93.48	93.41	93.44	Less than	0.1	0.1	0.9124
Oleomargarine IV.....	78.43	78.06	78.25	134.6	133.8	134.2	98.06	97.99	98.03	Less than	0.1	0.1	0.4989
Butter II (stale).....	40.35	40.19	40.27	227.3	226.9	227.1	89.27	89.33	89.30	4.175	4.163	4.169	9.736
Butter III (stale).....	33.44	33.74	33.59	233.4	233.6	233.5	89.48	89.60	89.54	3.749	3.741	3.745	26.01

While one viscosimeter may be used for many liquids, where a long series of measurements are to be made with substances of similar viscosity it is more practicable to construct one which will allow reasonable times of flow. Therefore, for the measurement of these fats, a viscosimeter was constructed with a very short capillary tube, and its constants were determined by using a glycerol-water mixture, the viscosity of which was measured in an instrument adapted to liquids of the viscosity of water, and having a correspondingly longer capillary tube.

Calibration of the viscosimeter used for the fats gave the following results:

Length of capillary (approx.).....	1.8 cm.
Volume of liquid passing through the capillary.....	2.76 cc.
Pressure correction.....	± 0.20 cm.
$\pi r^2 l$	0.000004916
$\pi r^2 l$	0.03286

The times of flow for the various fats and at different temperatures varied from about ten to two minutes.

The results are given in the tables which follow. Together with the viscosities are presented the fluidities, these latter being calculated by taking the reciprocals of the average viscosities. All viscosity results are expressed in C. G. S. units.

From the results given in the tables several conclusions may be drawn. In the first place, as would be expected from the fact that oleomargarine is more largely made up of the glycerides of the higher aliphatic acids, the margarines are considerably more viscous than butter. Wender¹ seemed to consider that there was but little variation in the viscosity of different butter samples, while the viscosities of margarines from various sources differed widely. This work, however, shows that an accurate instrument can detect variations in different grades of both products, and that slight changes in composition affect the viscosity of these fats to as marked an extent as they do the other constants determined. In general, the lower the viscosity the purer is the butter, and if a high viscosity is found, adulteration by beef or other fats

to the fact that it is the poorest sample. Samples III and IV have the lowest viscosity and are shown to be the best butters by their high content of soluble and volatile acids.¹

TABLE II—DENSITIES

Sample	40° C.	65° C.	90° C.
Butter I.....	0.9063	0.8901	0.8745
Butter II.....	0.9053	0.8896	0.8722
Butter III.....	0.9026	0.8865	0.8716
Butter IV.....	0.9026	0.8859	0.8720
Oleomargarine I.....	0.9026	0.8894	0.8711
Oleomargarine II.....	0.8989	0.8837	0.8666
Oleomargarine III.....	0.8997	0.8853	0.8666
Oleomargarine IV.....	0.9024	0.8867	0.8682
Butter II (stale).....	0.9069	0.8890	0.8730
Butter III (stale).....	0.9061	0.8892	0.8720

In connection with the change of butter on standing several interesting observations were made. If the butter fat was separated from water and curd, it became rancid very slowly, and after standing for considerable time at room temperature no appreciable change in viscosity could be detected. Consequently some of Samples II and III were allowed to grow rancid before removing the water and curd. The former stood about two months and the latter as many weeks. As shown in Table II, the samples which stood the longer decreased in viscosity, while the others

TABLE III—VISCOSITY RESULTS AT 40°

Sample(a)	Viscosity			Fluidity
	Down	Up	Av.	
Butter I.....	0.3244	0.3249	0.3247	3.080
Butter II.....	0.3228	0.3211	0.3219	3.107
Butter III.....	0.3080	0.3092	0.3086	3.241
Butter IV.....	0.3024	0.3025	0.3025	3.306
Oleomargarine I.....	0.3576	0.3605	0.3591	2.785
Oleomargarine II.....	0.3582	0.3584	0.3583	2.791
Oleomargarine III.....	0.3476	0.3464	0.3470	2.882
Oleomargarine IV.....	0.3352	0.3353	0.3353	2.982
Butter II (stale).....	0.3177	0.3171	0.3174	3.151
Butter III (stale).....	0.3105	0.3111	0.3108	3.218

(a) Butter samples I and II cost 33 cents a pound; III, 38 cents; IV, 30 cents. Oleomargarine samples I, II and III, 25 cents; and IV, 15 cents, increased. From the Reichert-Meissl number it is evident that Sample II lost considerably more of its volatile acids than Sample III. This seeming dis-

¹ It may be noted that Sample IV, purchased in the same market as Sample III at less cost, is shown to be the better of the two.

crepancy may be accounted for in the following manner: The butter which was kept for the shorter interval of time gave off some of its volatile acids due to hydrolysis, and the higher acids remained for the most part unchanged. This would increase the relative per cent of these higher acids and consequently the viscosity. The other sample, which became very stale and of a pasty consistency, lost much more of the volatile acids as shown by the constant and we should expect its viscosity to be so much the

If the above inferences are correct, it is very probable that the viscosity of butter increases with time to a maximum, and then decreases on putrefaction. The suggestion is of sufficient interest to warrant further investigation.

The viscosity results in general bear out Bingham's¹ views concerning the relations between viscosity and

TABLE IV—BUTTER-OLEOMARGARINE MIXTURES—I

C. temp.	Viscosity 100 Per cent Butter			Fluidity
	Down	Up	Av.	
40°.....	0.3244	0.3249	0.3247	3.080
50°.....	0.2289	0.2292	0.2291	4.365
60°.....	0.1666	0.1667	0.1667	5.999
70°.....	0.1257	0.1258	0.1258	7.949
80°.....	0.09817	0.09816	0.09817	10.19
90°.....	0.07847	0.07857	0.07852	12.74
95 Per cent Butter				
40°.....	0.3278	0.3262	0.3270	3.059
50°.....	0.2303	0.2296	0.2300	4.348
60°.....	0.1677	0.1678	0.1678	5.964
70°.....	0.1265	0.1264	0.1265	7.905
80°.....	0.09881	0.09858	0.09870	10.14
90°.....	0.07863	0.07891	0.07877	12.70
90 Per cent Butter				
40°.....	0.3268	0.3269	0.3269	3.059
50°.....	0.2303	0.2302	0.2303	4.342
60°.....	0.1684	0.1680	0.1682	5.946
70°.....	0.1275	0.1283	0.1279	7.818
80°.....	0.09889	0.09847	0.09868	10.14
90°.....	0.07946	0.07946	0.07946	12.59
75 Per cent Butter				
40°.....	0.3326	0.3323	0.3325	3.008
50°.....	0.2340	0.2343	0.2342	4.270
60°.....	0.1707	0.1709	0.1708	5.856
70°.....	0.1292	0.1290	0.1291	7.747
80°.....	0.1009	0.1011	0.1010	9.902
90°.....	0.08094	0.08088	0.08091	12.36
50 Per cent Butter				
40°.....	0.3403	0.3381	0.3392	2.947
50°.....	0.2391	0.2404	0.2398	4.170
60°.....	0.1756	0.1745	0.1751	5.712
70°.....	0.1346	0.1350	0.1348	7.418
80°.....	0.1033	0.1035	0.1034	9.672
90°.....	0.08310	0.08277	0.08291	12.06
25 Per cent Butter				
40°.....	0.3484	0.3481	0.3483	2.871
50°.....	0.2465	0.2475	0.2470	4.049
60°.....	0.1796	0.1800	0.1798	5.560
70°.....	0.1369	0.1369	0.1369	7.305
80°.....	0.1071	0.1062	0.1067	9.371
90°.....	0.08556	0.08548	0.08552	11.69
100 Per cent Oleomargarine				
40°.....	0.3576	0.3605	0.3591	2.785
50°.....	0.2520	0.2522	0.2521	3.976
60°.....	0.1844	0.1843	0.1844	5.424
70°.....	0.1398	0.1396	0.1397	7.157
80°.....	0.1094	0.1093	0.1094	9.139
90°.....	0.08758	0.08758	0.08758	11.42

greater. However, putrefaction of the casein also had commenced with a resulting change in the butter fat which lowered its viscosity without increasing the amount of volatile acids. These products, which do not influence the amount of volatile and soluble acids, may be acids of lower molecular weight than those from which they are derived, but which are insoluble and non-volatile. It should be noted that there is an increase in the quantity of insoluble acids in this last sample considered.

TABLE V—BUTTER-OLEOMARGARINE MIXTURES—II

C. Temp.	Viscosity 100 Per cent Butter			Fluidity
	Down	Up	Av.	
40°.....	0.3228	0.3211	0.3219	3.107
50°.....	0.2260	0.2264	0.2262	4.421
60°.....	0.1639	0.1643	0.1641	6.094
70°.....	0.1243	0.1245	0.1244	8.039
80°.....	0.09727	0.09686	0.09707	10.30
90°.....	0.07827	0.07838	0.07827	12.77
40°.....	0.3225	0.3226	0.3226	3.099
95 Per cent Butter				
40°.....	0.3239	0.3227	0.3233	3.093
50°.....	0.2274	0.2278	0.2276	4.393
60°.....	0.1657	0.1660	0.1659	6.027
70°.....	0.1249	0.1253	0.1251	7.995
80°.....	0.09782	0.09714	0.09748	10.26
90°.....	0.07791	0.07818	0.07805	12.81
90 Per cent Butter				
40°.....	0.3242	0.3255	0.3249	3.078
50°.....	0.2289	0.2298	0.2294	4.359
60°.....	0.1667	0.1674	0.1671	5.984
70°.....	0.1265	0.1266	0.1266	7.898
80°.....	0.09884	0.09889	0.09887	10.11
90°.....	0.07900	0.07897	0.07899	12.66
75 Per cent Butter				
40°.....	0.3297	0.3315	0.3306	3.025
50°.....	0.2323	0.2325	0.2324	4.303
60°.....	0.1700	0.1703	0.1702	5.874
70°.....	0.1283	0.1284	0.1284	7.787
80°.....	0.1003	0.0999	0.1001	9.990
90°.....	0.08049	0.08056	0.08053	12.42
50 Per cent Butter				
40°.....	0.3397	0.3401	0.3399	2.940
50°.....	0.2400	0.2408	0.2404	4.160
60°.....	0.1751	0.1755	0.1753	5.704
70°.....	0.1326	0.1327	0.1327	7.529
80°.....	0.1029	0.1028	0.1029	9.817
90°.....	0.08282	0.08274	0.08278	12.08
25 Per cent Butter				
40°.....	0.3486	0.3488	0.3487	2.868
50°.....	0.2460	0.2471	0.2466	4.055
60°.....	0.1814	0.1805	0.1810	5.525
70°.....	0.1375	0.1383	0.1379	7.251
80°.....	0.1062	0.1063	0.1063	9.407
90°.....	0.08576	0.08537	0.08557	11.69
100 Per cent Oleomargarine				
40°.....	0.3582	0.3584	0.3583	2.791
50°.....	0.2535	0.2541	0.2538	3.940
60°.....	0.1833	0.1833	0.1836	5.447
70°.....	0.1391	0.1391	0.1391	7.189
80°.....	0.1087	0.1085	0.1086	9.208
90°.....	0.08747	0.08743	0.08745	11.43

fluidity and composition. Briefly his hypothesis requires that the fluidity of absolutely unassociated liquids, which do not change on being heated, is a linear function of the temperature, and that mixtures of such liquids which do not interact should have additive fluidities. The fluidity temperature curves for one series of mixtures of butter and oleomargarine are shown graphically in Fig. II. It may be noted that they are nearly linear but that the slight curvature

¹ Z. physik. Chem., 66, 1, 1909.

indicates a certain amount of association in the fats. That this curvature is not a result of chemical change of the fats as they are heated from 40° to 90° is proven by the data in Table V. The viscosity of the pure

the fluidity is a linear function of the composition at any and all temperatures. Since the fluidity is the reciprocal of the viscosity it would be generally impossible, according to the theory, for viscosities to be additive. The viscosity curves for the mixtures given

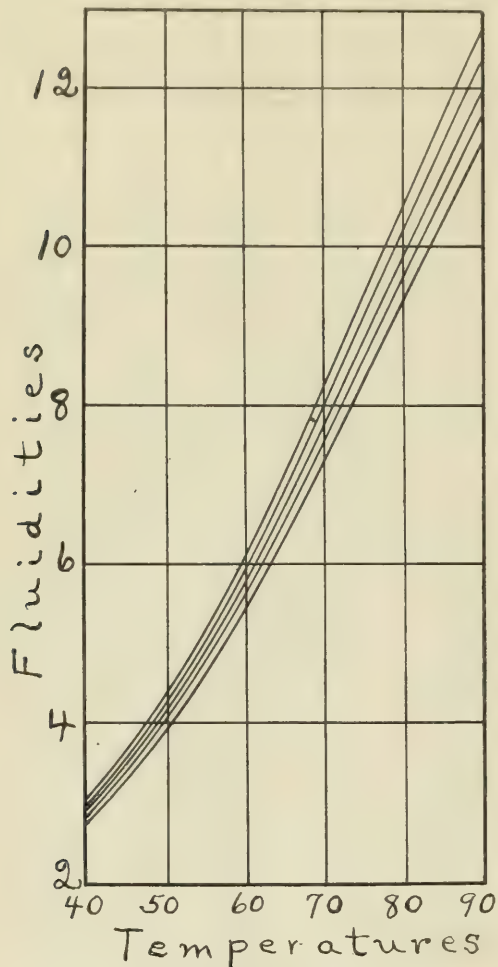


FIG. II. Fluidity Temperature Curves of Butter-Oleomargarine Mixtures—I

butter was determined after it had been so heated, and there is no change except what is well within the experimental error. Such association in the fats is very possible since it has been shown that esters are more or less associated. This same effect has been noted by one of us in work on fish oils.¹ By Fig. III it is seen that in accordance with the second part of the fluidity hypothesis as stated, the fluidities of the butter and oleomargarine mixtures are additive. Evidently then, any such association as was indicated is so insignificant as regards our results and conclusions concerning the additivity of the fluidities of these fats that it may be entirely disregarded. The slopes of the fluidity-temperature curves are practically identical, and it is safe to conclude that, in this case,

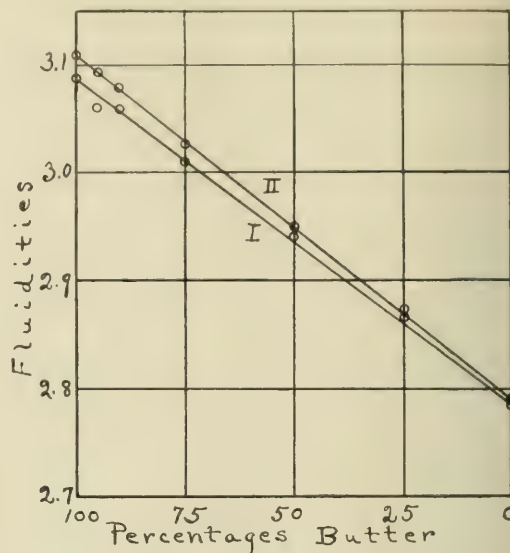


FIG. III. Fluidity Curves of Butter-Oleomargarine Mixtures, 40°

in Fig. IV show that this is also borne out experimentally, for very evidently a linear curve is not obtained. However, as has been repeatedly shown, when the viscosities of such viscous liquids as these fats are studied, no great divergence from the additive relationship is noticed when the viscosities of the

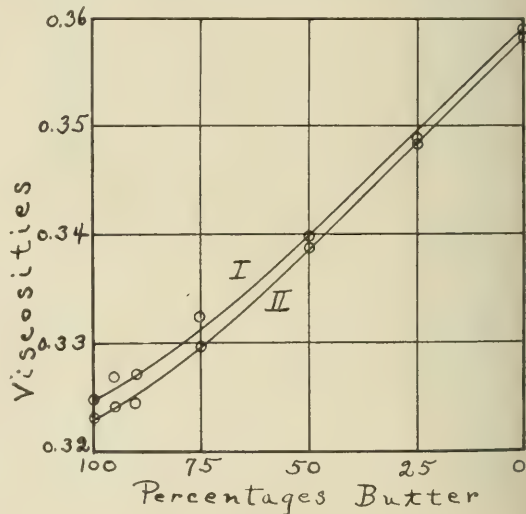


FIG. IV. Viscosity Curves of Butter-Oleomargarine Mixtures, 40°

components of the mixtures approximate each other. It was stated above that there was some variation in the viscosities of both butter and oleomargarine,

¹ Loc. cit.

yet there is a certain reliable mean value for both. These values, with the fluidities, are:

	η	ϕ
Butter.....	0.3200	3.125
Oleomargarine.....	0.3500	2.857

An adulteration of 10 per cent margarine in butter could be readily detected in the apparatus used in any case. Since pure butters from any one creamery vary very little, by finding the mean value for such products, admixture of a foreign fat of different viscosity could be shown if even only 1 per cent were so added.

SUMMARY

1. Oleomargarine fats are always more viscous than butter fats except, of course, where the viscosity of the former is greatly lowered by the introduction of large amounts of liquid fats as indicated by a chemical analysis.

2. On standing, the viscosity of butter probably increases to a maximum due to a loss of volatile acids, and then becomes less viscous as putrefaction sets in.

3. Although the viscosities for both fats vary somewhat in products from different sources, the fluctuation is always about a mean value which might be assumed without great error as a standard.

4. The viscosities of the mixtures are not strictly additive.

5. The fluidities are practically linear functions of the temperature.

6. The fluidities of the mixtures are additive, so that these, and not viscosities, should be the basis for any comparison.

7. Assuming that the fluidity of butter does not vary more than 5 per cent in value, an adulteration of 10 per cent oleomargarine can be detected with assurance by the method of determination used.

CLARK COLLEGE
WORCESTER, MASS.

THE PROPERTIES OF WATERED MILK

By EDWARD W. LONG AND CLARENCE E. MAY

Received April 2, 1913

Much work in the detection of added water in milk has been done by the usual chemical methods. So far as the authors are aware, no extensive studies have been made of the changes met where hard well water instead of distilled water has been added to milk, or where sucrose has been added to watered milk to build up the refractometer reading, or where additions of sucrose have been made to whole milk serum to build up the immersion refractometer reading.

The standard composition of milk has been well established, and published results of numerous analyses of American cow's milk are well known.¹ In recent years the method of detecting watered milk has been largely a study of the deportment of the given sample of milk when the corresponding milk serum was prepared and examined with the Zeiss immersion refractometer. Various methods have been suggested

for the preparation of the milk serum prior to the examination of the refractive power of the serum. Villiers and Bertault,^{1,2} as early as 1898, devised a method using acetic acid for the removal of milk proteins. Matthes and Müller,³ in 1903, made use of the Zeiss immersion refractometer for the examination of the serum which they obtained from spontaneously soured milk. Leach and Lythgoe,⁴ in 1904, made use of the immersion refractometer in examining milk serum prepared by the Woodman method. To 100 cc. of milk at about 20° C., 2 cc. of 25 per cent acetic acid were added, well mixed and placed on a water bath at 70° C. for 20 minutes. The mixture was then cooled for 10 minutes in ice water and filtered. The main difference between their method and those formerly used was in the heating of the acid-milk mixture for longer times at lower temperatures prior to filtration. Baier and Neumann⁵ used an asaprolic acid mixture as the precipitating agent. The serum so prepared was examined with the Wollny milk fat refractometer. Ackermann⁶ used calcium chloride as the precipitating agent in the preparation of milk sera. With so many procedures available, it seemed desirable to compare the various methods on samples of known purity. This was done by Lythgoe and Nurenberg.⁷ They found some methods had certain advantages over other methods but for ease of manipulation and getting concordant results, the Woodman acetic acid method as used by Leach and Lythgoe was preferred.

Other methods that have been useful in the detection of added water to milk are dependent on the preparation of the milk serum and the using of this serum in various ways such as the determination of the specific gravity, the nitrate reaction with diphenylamine, the determination of the freezing point, the determination of the electrical conductivity and the determination of the index of oxidation.

Using the specific gravity method of examination, Bull⁸ found that in eight cases 5 per cent added water was distinguishable, in ten cases 10 per cent added water was distinguishable and in fourteen cases (all examined) 15 per cent added water was distinguishable. Although the method seemed more delicate than the refractometer method, the author felt the refraction method more reliable.⁹

Varying interpretations are given to the estimation of nitrates in milk as indicating the addition of water. They are mentioned here to complete the bibliography. Tillman¹⁰ claimed that water containing 10 mg. N₂O₅ per liter could be detected when added to milk in amounts equal to 5 per cent of the milk. Galvagno¹¹ claimed that the nitrate reaction was valueless, while

¹ Reference to Villiers and Bertault, *THIS JOURNAL*, **1**, 38.

² Villiers and Bertault, *Bull. Soc. Chim.*, **19**, 305.

³ Matthes and Müller, *Z. offentl. Chem.*, **10**, 173.

⁴ Leach and Lythgoe, *J. Am. Chem. Soc.*, **26**, 1195.

⁵ Baier and Neumann, *Z. Nahr. Genussm.*, **13**, 369.

⁶ Ackermann, *Ibid.*, **4**, 186; *Chem. Abstr.*, **1**, 1588.

⁷ Lythgoe and Nurenberg, *THIS JOURNAL*, **1**, 38.

⁸ Bull, *Ibid.*, **3**, 44.

⁹ Woodman, *J. Am. Chem. Soc.*, **21**, 503.

¹⁰ Tillman, *J. Soc. Chem. Ind.*, **30**, 44.

¹¹ Galvagno, *Chem. Abstr.*, **3**, 2838.

¹ Leach, Textbook, "Food Analysis," 2nd Ed., p. 127.

Rothenfasser^{1,2} concluded that the nitrate reaction was given too little rather than too much attention.

Fischer^{3,4} found the freezing point of whole milk to be fairly constant, and when the watering of milk was not greater than 5 per cent, he was not able to detect with certainty the presence of the added water. With greater degrees of watering he was able to notice differences in the freezing points of the mixtures.

Flohil,^{5,6} on the one hand, found that even with 20 per cent added water no marked change in the electrical conductivity sufficient to throw the sample of milk outside of the limit for undiluted milk was noticed, while on the other hand Binaghi^{7,8} maintained that the electrical conductivity afforded a valuable indication of the presence of added water.

Comanducci^{9,10} devised a method for the determination of the extent of watering or skimming of milk based on the fact that the number of cubic centimeters $N/10$ KMnO_4 (H_2SO_4) necessary to oxidize a given quantity of genuine milk was nearly constant. The author claimed that this method could be used to determine the percentage of water added or the percentage of cream removed, providing the milk had not been both watered and skimmed.

Further, Burr and Berberich¹¹ have proposed a method for determining the watering of milk by means of examining the ash content of the milk serum. They have found this figure to be in between 0.797 per cent and 0.817 per cent for whole milk and for naturally-soured milk the figure was quite constant.

Richmond¹² has found that the amount of water added to milk can be determined by adding the difference between the specific gravity of the sample and 1000 to the figure representing the percentage of fat in the milk. Unadulterated milk was found to give a value of 36, but 34.5 was considered a safer limit. This method is perhaps of less value.

In the present investigation, the authors have used the acetic acid method for the preparation of the milk serum. This involved treating 100 cc. of milk with 2 cc. 25 per cent acetic acid, mixing thoroughly and heating stoppered in a water bath at 70° C. for 20 minutes. Besides using the whole milk sera, we have used various dilutions of milk and have employed various temperatures for reading the Zeiss immersion refractometer.

Using a number of samples of milk, we have studied the effect of temperature on the readings when they were taken at 15° C. and each respective degree of temperature up through 20° C. The following results will serve as an example; corrected readings are given:

DILUTION	15° C.	16° C.	17° C.	18° C.	19° C.	20° C.
Whole milk.....	46.05	46.0	45.8	45.6	45.3	45.1
20 parts added water....	40.4	40.15	39.9	39.65	39.4	39.15
40 parts added water.....	33.8	33.7	33.55	33.3	33.1	33.0
60 parts added water.....	27.85	27.7	27.5	27.3	27.15	27.0

We have examined ten samples of milk obtained from a local dairy. The same milk on being diluted with water until the added water amounted to 20, 40 and 60 per cent, respectively, of the mixture was acidified and the serum examined with the refractometer. The following results were obtained at 20° C:

Sample	Whole milk	20 per cent	Diff.	40 per cent	Diff.	60 per cent	Diff.
	H ₂ O	H ₂ O		H ₂ O		H ₂ O	
1	46.45	39.4	7.05	33.3	6.1	27.05	6.25
2	45.6	39.15	6.45	33.0	6.15	27.0	6.0
3	45.2	39.05	6.15	32.8	6.25	26.8	6.0
4	45.8	38.2	7.6	32.8	5.4	26.9	5.9
5	44.1	37.1	6.0	32.5	4.6	26.8	5.7
6	43.5	37.9	5.6	31.5	6.4	26.4	5.1
7	40.9	35.4	5.5	30.3	5.1	25.3	5.0
8	44.2	38.2	6.0	32.2	6.0	26.2	6.0
9	42.5	36.8	5.7	31.0	5.8	25.7	5.3
10	43.1	37.4	5.7	31.3	6.1	25.8	5.5

The average differences in refractometer reading for each 20 parts of added water as shown by the above table was 5.88° on the scale of the Zeiss immersion refractometer.

In order to ascertain what differences there might be when well water instead of distilled water was used for dilution of the milk, a number of samples of milk were diluted with well water and distilled water, respectively. The following table shows the readings with the different waters:

DILUTION	Distilled water	Well water
Whole milk, 42.6		
20 parts added water.....	36.7	36.7
40 parts added water.....	30.9	31.0
60 parts added water.....	25.9	26.0

The well water used contained 0.030 gram of total solids per 100 cc. From the table it is evident that there is but little difference in the readings. From the different samples examined it seemed that with a water containing 0.030 gram solids per 100 cc. there was an increase of about 0.1° above the refractometer reading observed when using distilled water. This difference is scarcely large enough to exceed the error possible in making the readings.

SAMPLE A		
Amount of sugar per 100 cc.	Whole milk readings	Difference per gram of sucrose
Grams		
0.0	42.8	...
1.0	46.6	3.8°
2.0	50.6	4.0°
3.0	54.6	4.0°
SAMPLE B		
Amount of sugar	Whole milk readings	Difference per gram of sucrose
Grams		
0.0	44.15	...
1.0	48.00	3.85°
2.0	52.05	4.05°
3.0	56.1	4.05°

In studying the influence of sucrose added to milk, whole milk was adulterated with 1.0, 2.0, and 3.0 gram portions, respectively, of ordinary granulated sugar per 100 cc. of milk and treated in the usual way to prepare the corresponding sera. Great care was exercised in getting all the sugar dissolved and the solution well mixed. Fourteen samples of milk

¹ Rothenfasser, *Chem. Abstr.*, **3**, 2988.

² Rothenfasser, *Z. Nahr. Genussm.*, **18**, 353.

³ Fischer, *Chem. Abstr.*, **2**, 1166.

⁴ Fischer, *Pharm. Zig.*, **53**, 48.

⁵ Flohil, *Chem. Abstr.*, **5**, 3598.

⁶ Flohil, *Chem. Weekblad*, **8**, 605.

⁷ Binaghi, *J. Soc. Chem. Ind.*, **29**, 1404.

⁸ Binaghi, *Biochem. Zig.*, **26**, 60.

⁹ Comanducci, *Chem. Abstr.*, **1**, 1588.

¹⁰ Comanducci, *Gazz. chim. ital.*, **36**, II, 813.

¹¹ Burr and Berberich, *Chem. Abstr.*, **2**, 3115.

¹² Richmond, Leffman and Beam, "Food Analysis," p 216 (reference).

yielded an average increased reading of 3.98° on the immersion refractometer scale for each gram of sugar per 100 cc. of milk. The average difference per gram of sucrose was approximately the same whether 1.0, 2.0 or 3.0 grams per 100 cc. of milk were used. The above will serve as representative samples.

Seventeen samples of milk were adulterated by additions of sugar and water. The samples were prepared by filling 100 cc. flasks with milk, withdrawing 20 cc. by means of a pipette, adding 1.0, 2.0 and 3.0 grams, respectively, of ordinary granulated sugar, dissolving and mixing the sugar solution carefully and then filling to the graduation mark with water. The samples were then heated with acetic acid as usual for defecation. In 17 samples, an average difference of 4.02° instrument reading per gram of sugar added was obtained. Following this, samples of whole milk were diluted to contain 60 parts milk and 40 parts of added water. Five samples gave an average difference in reading of 4.1° instrument reading for each gram of sugar added per 100 cc. of milk. Five samples of milk containing 40 parts of milk and 60 parts of added water yielded a difference of 4.04° (average) for each gram of sugar added.

The average difference in reading produced by a gram of sugar added per 100 cc. of milk calculated on the total 41 samples including whole milk, milk containing 20 parts added water, 40 parts of added water and 60 parts of added water, respectively, per 100 cc. of milk-mixture, was 4.03° . From these results it seems that 1 gram of granulated sugar added to 100 cc. of milk raises the refraction of the serum about 4° and no great difference is observed when either whole milk or watered milk is used. If this increasing figure is used together with the decreasing figure (2.9°) representing the refractometer reading produced by 10 per cent added water, one should be able to adjust the two figures so that the refractometer reading on the serum would come near that observed for unadulterated milk. Thus by adding the proper amount of sugar, the serum of the watered milk should be capable of yielding a refractometer reading approaching the normal milk before adulteration. We calculated with this in view and found that for every 10 per cent of water added, 0.725 gram granulated sugar (commercial grade) such as we were using had to be added to each 100 cc. of milk in order to make the adulterated sample of milk give the same refractometer reading as the original whole milk.

The following data was obtained from an actual sample of milk that showed a refractometer reading of the serum to be 44.15° and contained total solids amounting to 14.48 per cent. On watering this sample of milk until we had a mixture containing 80 parts of milk and 20 parts of added water, and adding 1 gram of granulated sugar, by calculation, we should have had a mixture yielding a serum with a refractometer reading of 42.35° . By actual experiment, we found 42.15 as the observed reading. Adding 2 grams of sugar per 100 cc. of milk-mixture should have yielded a refractometer reading of 46.35° . By observation, the actual reading was 46.1° . Adding 3 grams of sugar

to 100 cc. of the milk should have given us a serum with a refractometer reading of 50.25° . Exactly this figure was found by experiment.

The experimental part checked fairly well with the calculations. Other samples of milk with which we worked varied from the calculated value as much as 0.5° but the majority of the samples gave readings within closer range of the calculated values.

The sample of milk just described in detail although watered and sugared (1.0 gram per 100 cc.) yielded a refractometer reading safely above the standard usually associated with whole milk. The total solids in the diluted milk, after treatment with sugar, would have been 12.58 per cent, a figure exceeding the usual standard. The milk originally mentioned contained 5 per cent fat. Even on dilution this resulting figure would have been above the standard for butter fat. It is evident that the milk in question when diluted so as to contain 20 per cent added water and 1 gram of granulated sugar for every 100 cc. of watered milk, on being examined in the usual way would have given results that might have baffled the chemist in detecting the added water. Unless the sucrose tests had been applied, the sample might have been passed as unadulterated milk.

It can be shown that this form of milk adulteration is a profitable thing. At the rate of 1 gram of sucrose to 100 cc. diluted milk containing 80 parts of whole milk, one quart of the milk would require 0.025 pound of granulated sugar to bring the refractometer reading up to its original value. With sugar at 6 cents a pound and milk at 8 cents a quart, 0.15 cent spent for sugar would yield a return of 2 cents. The adulteration can be thus carried on profitably by the milk dealer if he is able to escape the chemist's sucrose tests.

CONCLUSIONS

1. The Zeiss immersion refractometer method of testing milk serum is doubtless the most practical method for the detection of water addition, but this method is far from infallible when used alone.
2. This work indicates that for every 10 per cent of water added to milk, the serum when prepared by the acetic acid method gives a refractometer reading about 2.9° lower than the unwatered milk.
3. The addition of 1 gram of granulated sugar to 100 cc. of milk, watered or unwatered, will raise the refractometer reading of the serum about 4° .
4. The adulteration of milk by watering and sugaring can be profitably carried on by adjusting the amounts of the adulterants and adding them to the milk that is well above the standard in solids and fat.
5. This work was carried out to find the actual importance of the desirability of detecting cane sugar as a milk adulterant. It seems that in examining commercial samples of milk it is well worth the chemist's trouble to look out for the presence of this form of adulteration.

THE DETERMINATION OF NITROBENZOL IN PEANUT OIL¹

By H. J. LUCAS

Received March 18, 1913

In the regular routine work of this laboratory, it became necessary to determine the amount of nitrobenzol present in certain varieties of peanut oil on the market. Because of its cheapness, a very large amount of this oil is consumed by the people of Porto Rico, especially the poorer classes, as a substitute for olive and other higher-priced oils. Inspection showed that a considerable percentage of the oil on the market was adulterated by the addition of nitrobenzol, which has been added for the purpose of giving a pleasant odor, and of deceiving the purchaser into thinking that the product was oil of bitter almonds. An examination of these products led to the working out of the following method.

Nitrobenzol is easily volatile with steam, and can be distilled from an oil by this means. However, experiments showed that there is considerable loss from this procedure: (1) because, it is very difficult to remove the last portions, and (2) because there is a continual, although slight loss by volatilization as is evidenced by the pronounced odor of the distillate. Since the distillation must be carried on for some time this continual volatilization causes an appreciable loss.

Nitrobenzol is easily reduced to aniline in hydrochloric acid solution by such reducing agents as stannous chloride, and metals. Attempts were made to recover this aniline by distillation with steam, but the same difficulties were encountered, as mentioned above. However, by the use of suitable immiscible solvents it was found that the aniline could be separated from the oil, evaporated to dryness from a hydrochloric acid solution, and weighed as aniline hydrochloride. Although the method does not give a complete recovery of nitrobenzol, it is so nearly so that for practical purposes it may be considered as quantitative.

To peanut oil, free from nitrobenzol and aniline, were added varying amounts of nitrobenzol, giving mixtures containing from 0.125 per cent to 1.000 per cent of the latter. These were then analyzed according to the following method: Thirty grams of oil containing nitrobenzol are weighed into a counterpoised, glass-stoppered Erlenmeyer flask of 150 cc. capacity. Five grams of zinc dust are added, and the oil gently agitated in order to distribute the finely divided metal throughout the mixture. Ten cc. of concentrated hydrochloric acid are then poured in, and the whole mixed quickly and thoroughly by three or four rapid whirls. Finally, 10 cc. of water are added, and the entire contents shaken vigorously, care being taken to avoid loss, since the heat development may cause the stopper to loosen.

Should the odor of nitrobenzol disappear within a few seconds, the amount of same present is very small, and but little more shaking is required for complete reduction. If, however, it persists for over three minutes, the amount is so large that continual shaking for fifteen minutes is necessitated. In either

event, at the end of this time the liquid contents of the flask are transferred to a separatory funnel by means of 50 cc. of ether and 25 cc. of water, care being taken to leave behind in the flask as much of the undissolved zinc as possible, which is washed into a second separatory funnel with 25 cc. of ether and 25 cc. of 5 per cent hydrochloric acid solution. The aqueous layer from the first separatory funnel is filtered through a wet filter into a third, and that from the second into the first. The contents of the second are then washed with 25 cc. and 10 cc. of 5 per cent hydrochloric acid, in two successive portions, which are, in turn, used for washing the oil-ether mixture in the first. The separate extractions and washings should be performed by shaking for two minutes, cautiously, as an emulsion is very liable to form if the shaking is done vigorously. The filtrate is a perfectly clear solution of zinc chloride and aniline hydrochloride in dilute hydrochloric acid, with traces of oil which passed through the filter.

This is now allowed to run slowly into 50 cc. of strong sodium hydroxide solution (100 grams of sodium hydrate to 150 cc. of water) which must be kept cool and shaken constantly. It was found very convenient to have the alkali in another separatory funnel. The resulting solution should be clear, or nearly so. The aniline separates as an oily layer, if the amount present is considerable, and the zinc remains dissolved as sodium zincate. Extraction with ether is made, using 60, 40, 30 and 20 cc., and pouring off from the top into a perfectly clean and dry separatory funnel. If, after standing for half an hour, small drops of water should be visible on the inner wall, the ether must be transferred to another, thus securing a solution of aniline free from inorganic salts. Final extraction is now made, using 4, 3, 2 and 1 cc. of 10 per cent hydrochloric acid solution successively, and shaking each time for 2 minutes. The acid extractions are evaporated on the water-bath in a tared platinum dish, which is kept covered until all the ether has boiled away and danger from loss by spattering has ceased.

PEANUT OIL									
SAMPLE TAKEN				RECOVERED					
No.	Grams oil	Per cent $\text{C}_6\text{H}_5\text{NO}_2$	Gram $\text{C}_6\text{H}_5\text{NO}_2$	Gram $\text{C}_6\text{H}_5\text{NH}_2$ HCl	Gram $\text{C}_6\text{H}_5\text{NO}_2$	Per cent $\text{C}_6\text{H}_5\text{NO}_2$	Per cent recovery	Weight non-volatile residue, Mg.	
1	30	1.000	0.3000	0.3030	0.2879	0.960	96.0	0.2	
2	30	0.500	0.1500	0.1521	0.1445	0.482	96.3	0.0	
3	30	0.250	0.0750	0.0728	0.0692	0.230	92.2	0.7	
4	30	0.250	0.0750	0.0729	0.0693	0.231	92.4	0.0	
5	30	0.125	0.0375	0.0371	0.0352	0.117	94.0	0.6	
LARD OIL									
6	30	1.000	0.3000	0.2960	0.2812	0.937	93.7		
7	30	0.500	0.1500	0.1486	0.1412	0.471	94.1		

The evaporation must be watched very carefully at the finish, the dish being removed just before dryness is reached, at a point where the whole mass will just crystallize when allowed to cool. If carried further, there is danger of loss by volatilization. The residue is dried to constant weight in a soda lime desiccator: this requires from 16 to 35 hours, depending upon the amount of residue. On ignition at a low red heat,

¹ Published by permission of the Director of Sanitation, Government of Porto Rico.

the amount of inorganic material is obtained, which, when subtracted from the total residue, gives the weight of aniline hydrochloride.

The accompanying table gives the results of analyses of mixtures of peanut oil and nitrobenzol of known strength, and also two of lard oil and nitrobenzol.

CHEMICAL AND BROMATOLOGICAL LABORATORY
SAN JUAN, P. R.

THE DETERIORATION OF SODA WATER DUE TO MICRO-ORGANISMS

By N. P. SHERWOOD AND C. C. YOUNG

Received June 2, 1913

During the last two years many letters have been received at this laboratory from soda water bottlers asking for information relative to the cause and prevention of the so-called "diseases" of soda water. In a few instances, at least, bottling works have been forced to close down their business, owing to the fact that the product put out by them continually "went bad." As it is of economic importance to the various soda water manufacturers throughout the country and indirectly of interest to the consumer, an invitation was extended to various bottling works in the state to send in to the laboratory samples of spoiled soda water whenever found. Accordingly, a large number of samples were received and examined. It was found that the spoiled beverages may be classified into three groups, namely: *First*, stringy pop; *Second*, pop with sediment and turbidity; and *Third*, pop in which sufficient fermentation had developed to blow off the caps or break the bottles. The authors have been unable to find records of any previous work on this subject.

A microscopical examination of several samples revealed the fact that stringy pop, in these particular cases, was caused by the presence of a one-celled algae, "Tetraspora." Data on file in the water laboratories showed that the water supply used in the manufacture of the soda water was infested with an excessive growth of this algae. The stringiness was due to the mucilaginous nature of the cell walls which hold the cells together in large colonies. It can readily be seen that any algae-infested water, used directly, will give the manufacturer trouble. The use of distilled water is the best and easiest solution of this difficulty. Filters will not protect the bottler from this trouble entirely as the algae grow through the filters.

Those samples of soda water, showing only sediment and turbidity or in many cases sediment alone, were shaken, carefully opened and portions of the contents plated out on agar and other portions were inoculated into saccharose and dextrose broth fermentation tubes. Microscopical examinations were also made of the sediment settling to the bottom of the bottle. The agar plates showed the presence of 30,000 to 45,000 yeasts per cubic centimeter while the microscopical examination of the sediment established the fact that it was made up, in every case, of yeasts. Several strains of bacteria were isolated along with the yeasts and kept for further study as will be described presently.

While many bottlers reported losses due to blowing off of caps to bottles no samples thus affected were obtained, but instead a successful attempt was made to

produce this effect by inoculating various kinds of soda water under normal conditions, with three laboratory strains of saccharose fermenting colon organisms, which had been isolated from polluted water and sewage. The yeasts and bacteria isolated from samples showing sediment and in some cases marked turbidity were separately inoculated each into a respective set of samples to check up the cultural and microscopical findings mentioned above. A set of controls was also carried. Two varieties of soda water were used in these experiments, Cocoa Cola and Cream. These were inoculated in sets of four bottles each with the following organisms:

Set Lab. No.

1	101	Saccharose fermenting colon organism.			
2	102	Saccharose fermenting colon organism.			
3	107	Saccharose fermenting colon organism.			
4	5428	Yeast (from ginger ale).			
5	5429	Saccharose fermenting bacillus.	Acid.	No gas	(from cream pop).
6	5432	Yeast (from lemon soda).			
7	5426	Saccharose fermenting bacillus.	Acid.	No gas	(from ginger ale).
8	5427	Saccharose fermenting bacillus.	Acid.	No gas	(from ginger ale).
9		Controls.			

NOTE: These experimental samples were bottled under normal factory conditions, with the exception that all bottles were sterilized.

When soda "goes bad" it does so almost invariably in hot weather, hence these bottles were placed in an incubator and kept at 37° C. for a week and then placed at room temperature and kept for several months with the following results:

SET	ACTION
1	Developed slight turbidity only.
2	Developed slight turbidity only.
3	Developed slight turbidity and sufficient gas produced to lift caps.
4	Heavy sediment produced, made up of yeast and cap from one bottle lifted.
5	Turbidity only.
6	Sediment yeast.
7	Turbidity only.
8	Contaminated with yeasts, probably from bottling machine.
9	Normal pop. No sediment or turbidity.

NOTE: Active-gas producing colon organisms and yeast were found.

It would seem from the above that while not all strains of saccharose fermenting colon organisms will produce sufficient gas to lift the caps on the bottles, yet an extremely good gas-producing strain may bring this about and also that some strains of yeast will produce this result. Hence the use of polluted water might, in addition to endangering the health of the consumer, render the produce unsalable owing to presence of large numbers of colon organisms.¹ In a previous paper by the authors, it was noted that when a certain strain of *B. coli* was inoculated into pop it rapidly died out; this, however, was a non-saccharose fermenting organism and did not produce turbidity in the pop.

It is also evident from these experiments that sediment may be produced in pop owing to presence of certain wild yeasts, and also that any bacteria which ferment saccharose with the production of acid but no gas may render the pop turbid and unsalable.

Inasmuch as it is an established fact that algae grows only in the light it is important that all distilled

¹ THIS JOURNAL, 3, 495

water stored in the bottling plants should be kept in the dark.

We wish to suggest to bottlers that they discard wooden kegs as they have been found to be carriers of yeasts and undesirable bacteria even after attempts have been made to sterilize them with hot water. Salt-glazed pottery, where substituted for wooden

receptacles, are very easily sterilized and have given excellent results in practice. Every effort should be made to keep all materials covered to prevent the entrance of these organisms from the air.

BACTERIOLOGICAL LABORATORIES
UNIVERSITY OF KANSAS
LAWRENCE

LABORATORY AND PLANT

SOME PROJECTION EXPERIMENTS WITH SPECTRA¹

By H. E. HOWE

Received May 3, 1913

The development of projection apparatus within the last few years, producing forms with which work of precision can be done, naturally led to the use of such instruments in fields where projection heretofore has not entered. The mention of projection apparatus recalls to the minds of most people simply the process of projecting lantern slides, but the physicist has for a long while used projection in lecture experiments and laboratory work. Of late the biologist has found it most useful for lantern slides, opaque ob-

A lecture given by Dr. C. E. Kenneth Mees on the "Nature of Color" before the Rochester section of the American Chemical Society suggested these simple experiments, for in that address Dr. Mees used the Zeiss complementary color projection apparatus, the principles of which are used in the instrument I have here.

However, the Zeiss instrument is too difficult to set up and has other objections which made a simplification very desirable for our purposes. Mr. W. L. Patterson, of the Bausch & Lomb Optical Co., therefore undertook the construction of a complementary color apparatus which would have the form of a con-

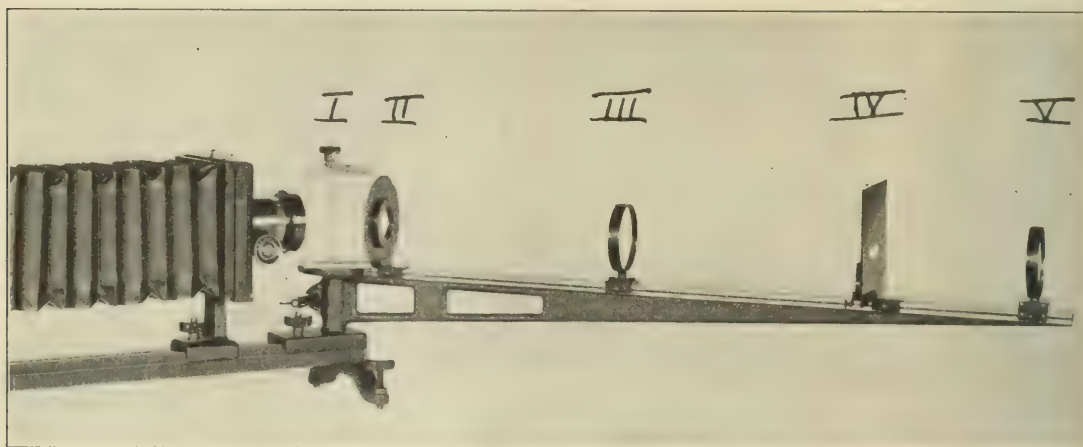


FIG. 1

jects, and for microscopical projection, not to replace the table microscope but as an accessory. It has always seemed to me that the chemist could use projection (more especially in lectures) profitably and to a large extent if he would but work out a few experiments as a beginning, and add to them as his familiarity with the projection suggests other experiments. The first of these chemical experiments with the aid of projection were given by Dr. Frank B. Kenrick, of the University of Toronto, and myself, at the general meeting of this Society at the Washington meeting, and the few experiments I now have to offer are more in the line of physics but have an application to the teaching of chemistry especially in qualitative analysis where the spectroscope is used for the identification of certain elements.

¹ Paper presented at the general session of the Milwaukee meeting of the American Chemical Society, March 25, 1913.

venient attachment which can be used on any of the well-known Balopticons possessing a lathe bed. The result was a light and easily adjustable apparatus which is shown in Fig. 1.

The projection apparatus consists of a Balopticon set up for lantern slide projection but with an extra standard, upon which the adjustable slit is carried, placed between the condenser system and the projection lens and to the bed of this Balopticon, the complementary color apparatus is attached as illustrated. This instrument consists of a short optical bench which may be adjusted to any angle with reference to the bed to which it is attached and which supports the following accessories:

- I. A bottle prism for holding carbon bisulfide or any other liquid.
- II. An Iris diaphragm and light shield.

III. Lens which images Iris diaphragm on the projection screen.

IV. A screen with rectangular opening and supporting slides having both cross and vertical movements.

V. A lens which may be swung in or out of the optical axis, depending upon whether a disc in which the spectrum is reunited is desired or the spectrum itself.

The optical bench is turned about the axis of this support until the angle of minimum deviation of the prism is found when it is clamped in its position. When set up we obtain a brilliant spectrum of the carbon arc in rectangular form just as the student sees it in the spectroscope.

The screen IV has a vertical and cross slide with clips for holding small deflecting prisms. By moving these prisms to any point desired that portion of the spectrum can be deflected so that with V in position we get two images of the Iris diaphragm, II, on the screen. One of these images will be the color of that portion of the spectrum which has been deflected while the remainder of the spectrum is shown in the other disc; where the discs overlap we see white light. By using two prisms, one of which deflects the light downward and the other upward from the normal we can obtain three discs of light. The prism carrier may be moved across the spectrum by means of the cross slide and complementary colors clearly demonstrated. (This was then shown.)

The absorption spectra of colored glasses or of solutions can be satisfactorily shown by placing the colored glass or cells of the solution in the path of light just

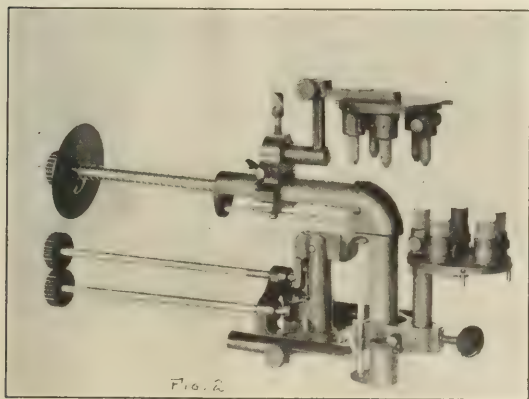


FIG. 2

back of the slit; that is, between slit and the light source, near the slit. Any spectroscope cell can be employed. Those which I use are twenty-five millimeters in thickness, provided with a glass stopper to prevent evaporation and consist of a glass ring cemented between two square plates which act as a support. With these cells I have found the following concentrations to be satisfactory: uranium sulfate 15 per cent, potassium bichromate $2\frac{1}{2}$ per cent, potassium permanganate $\frac{1}{32}$ part per 1000, copper and ammonium sulfate $2\frac{1}{2}$ per cent, didymium

nitrate 30 per cent. These salts were chosen at the suggestion of Dr. Mees as six which gave very characteristic absorption spectra, and it is obvious that the absorption spectrum of any solution can be quickly demonstrated to an entire class in this manner.

The emission spectra of elements is shown with the same apparatus by introducing salts into the carbon arc as is well known. The old method of changing carbons for each element to be projected must be followed if pure spectra are to be obtained, but the inconvenience of changing hot carbons is overcome by the holder in Fig. 2.

Revolving holders for the carbons carrying the salts are not new, but in this design we have the revolving holder for the negative as well as the positive carbon, since if both carbons are not changed sufficient oxide is deposited on the negative carbon to give an impure spectrum with the next salt demonstrated. With work with direct current the best results are obtained by having the positive pole on the lower carbon which carries the salt. To eliminate the spectrum of the carbon arc, a vertical arc is used and the carbons separated until the image of the arc and the spectrum of the arc fall above and below the rectangular opening in the screen IV, Fig. 1. In this position the vapor of the salt becomes the source of illumination, and we have upon the screen the characteristic spectrum of the salt just as we see it in the spectroscope. In this form of holder one passes successively to each of the five different salts with the minimum inconvenience and by turning the upper carbon holder each time the lower one is turned, has in reality a fresh pair of carbons for each demonstration.

The question of the best manner in which to introduce the salts in the arc next confronts us. The way in common use is to employ a carbon of the flaming arc type or to drill out the core of the soft-cored carbon A, Fig. 3, and then fill this hole with asbestos cement made up with the fluoride or chloride of the element. I have found this to give good results when sufficient care had been exercised in preparing the

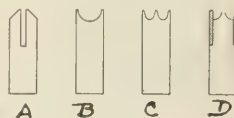


FIG. 3

carbon, but very frequently the substance melted and ran to the bottom of the cavity, leaving insufficient material for the arc to give a brilliant spectrum. There is also trouble in preparing a number of carbons if one wishes to demonstrate any number of salts. A solid carbon turned out as in B, Fig. 3, was next tried but in this case the arc would form at the edge of the crater and run around the carbon, making it impossible to keep it centered. This led to C, Fig. 3, in which it was hoped the arc would remain at the center where the little projection of carbon was left for the purpose, but this did not prove successful for the reason that the arc in following the line of least resistance would sometimes jump to the circumference. It, therefore, was little better than B.

Next a solid carbon was turned to the shape shown in D and a cup formed by placing a short piece of porcelain combustion tubing in the place indicated

by the shaded portion. While this process was successful in so far as keeping the arc centered was concerned and gave an easy method for introducing any salt into the arc, it had the serious objection that the glaze of the combustion tubing gave the sodium line in all spectra. Finally, fused quartz was substituted for the porcelain and the result is a satisfactory cup for the process. By using a carbon of small diameter in the upper holder there is no difficulty in striking the arc, even after the original carbon projection has been burned away. Any salt can be quickly introduced and the silica tubes serve for a number of burnings. Spectra of barium, strontium, calcium, lithium, and silver were found to be satisfactory for demonstration. (These spectra were then shown.)

The spectra of gaseous elements have not been projected, owing to the fact that sufficient illumination could not be secured. The transformer type of spectral tube, Fig. 4, as designed by Dr. P. G. Nutting overcomes this difficulty for, owing to its construction in which a large capillary is employed with corre-

spondingly large electrodes, a light 100 times as intense as that produced by the old tubes is secured. This type of transformer tube uses about 10,000 volts which I secure by means of a Clapp-Eastman transformer operating on an alternating current of 110 volts. This is an inexpensive and excellent transformer and together with the tube described gives us good illumination without noise. The holder for these tubes consists of a suitable piece of asbestos wood supported on a clamp which fits the optical bed. There is an asbestos wooden block on this which holds the tube supported by a brass plate in which the slit is cut. The plate

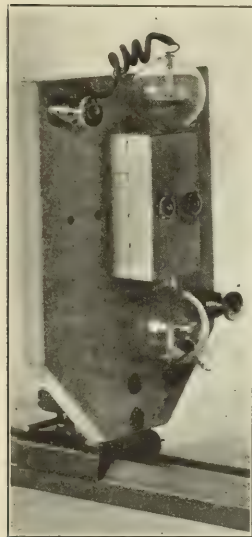


FIG. 4

is held in position by two posts with nuts. The holder also carries two binding posts so that connections with the platinum wires of the transformer tubes can be carefully made at leisure, leaving any hurried changes to be made with the feed wires at the large binding screws. The holder with the tube is placed in the same position as the slit for the other experiments. The helium, hydrogen, and neon tubes used were loaned by Dr. Nutting. (Spectra of the three elements were then shown.)

For the arc spectra a similar holder, Fig. 5, is provided, but in this case of slate since the resistance is such that the 10,000 volt current from the condenser will flow from one terminal to the other through asbestos wood. A porcelain hood with brass cap in

which the slit is cut is mounted to prevent light falling into the room and the metallic electrodes are fitted with pins as illustrated so that in changing from one set of electrodes to another it is only necessary to insert them as far as the pin will allow them to go and secure them with the set screws. The electrodes have chisel points.

Connections with the current are made at the binding posts. So far we have not been able to obtain a suitable screen for demonstrating the ultraviolet spectra of these arcs to any considerable number of people but hope to accomplish that later. In observing the spark spectra of metals in the ultraviolet, the projection lens is replaced by one made of quartz and the bottle prism of carbon bisulfide by a quartz Cornu prism.

Thus, we have simple devices for certain spectrum experiments which can be carried on so that an entire class may view the results simultaneously and also used as a supplement to the table spectroscope.

It is hoped that those interested in the subject will find the experiments useful in their work. I wish to give proper recognition to Dr. Mees and Dr. Nutting for the valuable aid rendered in working out the details of the experiments and offering valuable suggestions and to Mr. Patterson who is responsible for the designs of the special apparatus, carbon holders, supporters, etc.

BAUSCH & LOMB OPTICAL CO.
ROCHESTER, N. Y.

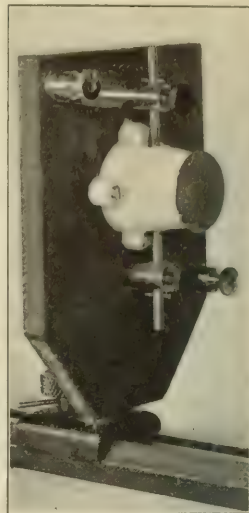


FIG. 5

A SHORT METHOD TO DETERMINE THE EFFICIENCY OF OXIDES FOR GAS PURIFICATION

By A. F. KUNBERGER

Received May 23, 1913

The gas engineer as a rule is not as much interested in how much total iron oxide is contained in a given batch or shipment of oxide as he is in how much hydrogen sulfide can be removed per ton or per bushel of oxide before it is saturated and requires renewal.

That the regular chemical analysis does not give him this required information is evident from the fact that one oxide containing almost twice as much Fe_2O_3 as another, may absorb but $\frac{1}{10}$ of the amount of H_2S absorbed by the latter, and it is the object of the present communication to describe the method developed and employed in this laboratory for the estimation of the efficiency of purifying oxides.

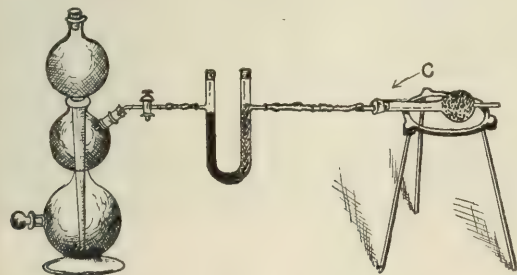
To determine the quantity of H_2S a given oxide would be able to decompose, the water formed by the reaction was absorbed in a weighed tube containing

fused CaCl_2 , as a preliminary experiment. It appeared evident, however, that these results must be incorrect unless the amount of moisture in the oxide could be correctly estimated before and after the test, so as to correct for the moisture originally contained in the oxide, and carried along by the water formed by the reaction. This is difficult, and requires time, and, owing to the rapidity with which some oxides revivify, it is almost impossible. Without this correction the method would be lacking in accuracy to such an extent that it would be of little value, and to avoid this the entire products must be weighed.

The results obtained were very satisfactory, and the method has been in use for over a year with good results. It enables one to determine in a very short time (about 1 hour), whether an oxide to be used, is very active, active, or indifferent.

The procedure is as follows:

A glass tube with a bulb at one end (see C in sketch) is most suitable to hold the oxide to be tested, but a



U-tube or almost any other tube compact enough so that it can be weighed on an analytical balance will answer.

In tube C a *ayër* is placed over the outlet to prevent any of the contents from passing through the little outlet tubing. On this cotton is placed enough small granular calcium chloride to fill the bulb; it is then covered with a thin layer of cotton to hold the calcium chloride in place.

Five grams of the oxide to be tested are next mixed with about 2 grams of coarse sifted sawdust and placed in the tube, and covered with another layer of cotton to prevent any of the contents from falling out at the stopper end of the tube. The stopper is then inserted. The entire tube is accurately weighed and the total weight noted.

A U-tube filled with calcium chloride to dry the hydrogen sulfide issuing from the generator is connected with the test tube by means of a piece of rubber tubing and the whole connected with the generator. A small piece of glass tubing closed at one end so as to leave only a hole the size of a small pinhole and placed between the U-tube and the generator regulates the flow of gas.

The hydrogen sulfide gas generated in the Kipp generator, and dried by passing it through the calcium chloride in the U-tube, is decomposed by the iron oxide in the test tube C, forming iron sulfide and water. The water formed is absorbed by the calcium chloride in the bulb of the test tube.

The test is carried on for 1 hour, after which time the test tube is disconnected and weighed. The gain in weight represents the amount of hydrogen sulfide absorbed, or rather decomposed, by the oxide. By dividing the amount of oxide taken, into this weight, the percentage of hydrogen sulfide decomposed can be determined, and from the latter the sulfur calculated.

The following analysis and fouling tests made with some oxides will illustrate how much more satisfactory results can be obtained by the fouling test than by chemical analysis alone.

Sample No.	No. 1 Per cent	No. 2 Per cent	No. 3 Per cent	No. 4 Per cent	No. 5 Per cent
Iron oxide.....	47.36	64.00	65.92	72.32	76.90
Total H_2S absorbed in 1 hour.....	22.01	19.85	10.80	2.66	2.80
Total H_2S absorbed per unit of Fe_2O_3	46.5	31.0	16.4	3.7	3.6
After revivification.....	21.34	3.5	3.34	1.66	1.58

Since the above fouling tests were borne out by results obtained on a large scale in the works, one is encouraged to believe it will greatly reduce the work of the chemist, and at the same time give information that usually can not be obtained from chemical analysis alone.

Some oxides are very active at the first fouling (when new), but revivification is slow and incomplete, and on second fouling they give far lower results. For this reason it is sometimes desirable to carry the test far enough to determine the total absorbing capacity of an oxide. This is particularly the case where a new oxide is to be introduced, as well as where new shipments are to be received. In this case it is advisable to keep the CaCl_2 and oxide in separate tubes, but they should be weighed together.

After the first fouling, the oxide tube is disconnected from the CaCl_2 tube, and air passed over it until completely revivified. To prevent an oxide which has the tendency to revivify very rapidly from getting too hot and consequently burning, thus becoming more or less inert, it is advisable to pass the air used for revivification over water so as to saturate it with water vapor.

After complete revivification, the tubes of oxide and CaCl_2 are again weighed and connected with the Kipp apparatus, and fouled a second time. This second fouling as a rule is sufficient to show how active the material is, for if the results of the second fouling are very close to those of the first, the material is very active, but the test can be repeated the same number of times as the oxide is revivified in practice: thus the entire capacity of the oxide can be determined before it is placed in service.

CHEMICAL LABORATORY
UNITED GAS IMPROVEMENT CO.
PHILADELPHIA

THE ELIMINATION OF RUBBER STOPPERS FROM THE VITRIFIED CLAY COMBUSTION TUBE BY MEANS OF TAPERED CLAY INLET AND OUTLET

Received June 13, 1913

By CHAS. MORRIS JOHNSON

In THIS JOURNAL, 5, 488, the writer published an account of a vitrified clay combustion tube with

tapered outlet designed by the author and manufactured at this works. The tube has been in successful operation for six weeks of twenty-four hour working days and is still in commission. Several more are now in use and mark a considerable reduction in cost of carbon determinations as the material from which the tubes are made costs less than 1 cent per tube.

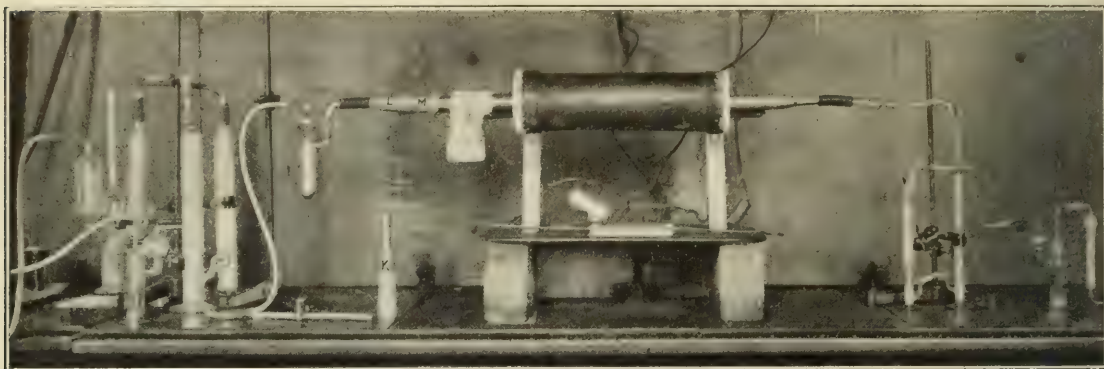
The advantage of the tapered outlet very soon suggested the making of a tapered clay inlet which is shown at K in the illustration and also at L-M.

The clay part of the inlet is a duplicate of the outlet end. The tube is charged and discharged by re-

pierced by the cylindrical surface of the combustion tube which makes only a single circle of contact between the stopper and the tube. The slip-over gives a tangential contact which provides innumerable circles of contact.

Further superiority of the tapered clay and rubber sleeve inlet is that, should the bore of the combustion tube tend to be elliptical instead of a true circle, the elasticity of the rubber sleeve will still give a pressure-tight connection on account of the large surface of contact.

Again, many combustion tubes offered by dealers are rejected because of grooves in the interior walls,



moving L-M which is connected to the main part of the combustion tube by means of the rubber sleeve M. This connection is a piece of $\frac{3}{4}$ inch bore, $\frac{3}{16}$ inch wall and $2\frac{1}{4}$ inches long, pure rubber tubing. This sleeve is more easily handled than a rubber stopper. The operator grasps L-M at the clay part L and slips it over the main part of the combustion tube and twists it firmly in place. The clay part L offers a substantial hold for one's hand and is absolutely safe. A glass taper would be dangerous as it might be crushed when grasped, causing a wound.

The slip-over connection is geometrically a tighter connection than a rubber stopper, for the reason that the latter affords an example of a conical surface

at the inlet or outlet ends, which make tight connections with rubber stoppers impossible. The tapered slip-over connection renders such tubes perfectly satisfactory.

The entire apparatus with the single exception of the little mercury valve tube attached to L-M is the author's design and shows but one rubber stopper at an unimportant point in the little KOH drying tube at the extreme outlet end of the combustion train. This could also be eliminated by a small glass taper or clay taper.

LABORATORY OF THE PARK WORKS
CRUCIBLE STEEL CO. OF AMERICA

ADDRESSES

EXPERT TESTIMONY—ITS MATERIALITY—CAUSES FOR ITS DISCREDIT—AND REMEDY¹

By JUDGE J. T. RONALD

Expert testimony does not always consist entirely of opinions. The bacteriologist *knows* whether microbes are in the water and whether germs are in the food; the toxicologist *knows* whether poison is found in the tissues; the metallurgist *knows* that certain clays contain aluminum and that it will bubble forth under certain heat; the chemist *knows* the results to follow certain conditions; the doctor *knows* the causes of many diseases and conditions; the constructive engineer *knows* the tensile

strength of various materials; the civil engineer *knows* levels, curves and volume of cuts and fills. All this is expert testimony, but this paper deals only with that class of expert testimony which consists entirely of opinions on questions of science or skill, given by persons learned or experienced therein. It constitutes the exception to the general rule of law, that opinions are not admissible in evidence.

Eminent jurists are on record in favor of the abolition of this exception and the rejection of all opinions as evidence. This, in my opinion, would be a serious retrogression, and would result, in many cases, in excluding from courts of justice material truth, and the consequent rendition of unjust judgments based on falsehood.

The field of judicial investigation, requiring the assistance

¹ Address delivered by Judge Ronald, of the King County Superior Court, before the Puget Sound Section, A. C. S., March, 1913.

of experts, is illimitable. Questions relating to human anatomy, diseases of the human body, derangement of the functions of the brain, the genuineness of handwriting, valuation of or damage to property, compliance with technical requirements of contracts, infringement of patents, causes of death, existence of mineral veins, customs of marine traffic, causes of this or that chemical, electrical or some other natural phenomena, of which the average lawyer, juror and judge possess no knowledge, are, in some form or other, subjects of daily investigation in our courts.

The further advancement of sciences in new and unexplored regions, supplanting last year's contested theories with this year's established facts, and evolving from last year's unlocked dark mysteries the dawning light of this year's progressive theories, thereby appreciably magnifying the importance of enlightening the trial tribunal with the best evidence which advancing science can produce, makes the testimony of the expert more and more a material aid to the ascertainment of truth. Nor must it be supposed that the expert in the scientific field deals altogether with mere theories.

While it is true that many of Nature's laws are not understood; that many conflicting systems of some of her branches of science have not been reduced to uniformity or exactness—thereby affording an ever fruitful source for conflicting theories, or for disagreements among contentious exponents, however sincere, yet, in the words of an eminent writer: "No one who is borne along by the irresistible current of modern inductive thought, can escape the conviction that in the realm of Nature, all things—all activities—conform to definite and immutable laws; that many of these laws scientists now understand and have formulated in terms of mathematical precision. The astronomer has scanned the heavens and read the glories of infinity; the geologist has studied the earth and found 'tongues in trees, books in running brooks, sermons in stones and good in everything.' Old ideas have perished in the retort of the chemist. A new world has been discovered by the microscope; everywhere has been found the infinite. In every direction man has investigated and explored, and nowhere on earth or star has he found the least interference with the external reign of Nature's laws."

A practical chemist can tell whether stains are of blood or rust, and if of blood, whether of man or beast. The experienced toxicologist can determine whether death be the result of poison; yet, upon true answers to these and many similar questions, justice itself, stern and exacting, or a human life may depend.

Such testimony is often the only means of arriving at the truth, and "When delivered with caution and without bias in favor of either party or in aid of some speculation and favorite theory, it becomes a salutary means of preventing intelligent juries from following a popular prejudice, and deciding a cause on inconsistent and unsound principles."

Yet, material as expert opinions are to the administration of justice, the courts are confronted by a condition where, whatever the causes, the evidence of the paid expert has very little, if any, value with judge or jury. It is admitted because the law allows such, and because nothing better can be had, but it is a common occurrence, after such testimony has been elaborated and at great expense introduced, to see juries who, instead of being enlightened and aided, are but bewildered and perplexed, and show their contempt by absolutely disregarding the whole mass thereof. "They do not attempt to weigh honors, learning, experience or standing of one expert contradicted by another. They do not attempt to compare relative value or reasonableness of conflicting expert testimony."

While conceding its importance, it is condemned by judges in general, by respectable legal text books and journals. It meets no praise in any recent decision—finds no welcome in any existing court. One author says: "There is a growing tend-

ency to look with distrust upon every form of skilled testimony."

An eminent writer and lawyer in an address before the Pennsylvania Bar Association in 1898 said: "It is patent to any one who chooses to inform himself that expert testimony, as now received in our courts, is looked upon by the public as an unmitigated farce and a nuisance."

The Supreme Court of Michigan (29 Mich. 4) says: "The experience of courts with the testimony of experts has not been such as to impress them with the conviction that the scope of such proofs should be extended. Such testimony is not desirable in any case when the jury can get along without it."

The Supreme Court of the United States (1 Curtis 439) says of it: "This species of evidence is less satisfactory than any other."

Nowhere is this state of affairs more deplored than among members of the profession themselves. *The Medico-Legal Journal* of June, 1912, of medical opinions, says: "The value and efficiency, and public utility of medical expert testimony has fallen into great disfavor among all classes of our people in a lamentable degree."

A well-known alienist, writing in the March number of the same journal, said of his own profession: "No class of specialists in any profession has been as bitterly assailed and severely criticized as the alienists. * * * They are the victims of public suspicion, of newspaper condemnation, and of the criticism of their own colleagues in the medical profession. * * * The shadow of suspicion universal and disquieting falls athwart the reputation of the alienist and, like a freak of the unreasoning elements, descends alike upon the just and the unjust."

Now, it is a bad condition of affairs when testimony so material, and in many cases absolutely indispensable, to the cause of truth and justice, should go upon its mission so tainted and discredited. There are underlying causes for this degradation, and before this class of evidence can have its due weight and effect it must regain public confidence; to do this the underlying causes must be removed.

Among lawyers generally, and judges and thoughtful writers on the subject, there exists great unanimity as to the principal causes responsible.

One contributing cause is often found in the lack of qualification of the expert himself, or in the ignorance of counsel, and sometimes in both. Courts are often too lax in applying the tests of qualification. Instead of requiring the proffered expert, as a pre-requisite to giving his opinion, to show he possesses special knowledge and skill concerning the particular subject under investigation, all that is generally required of him is to say he possesses some knowledge of the subject, whereupon the Court indulges the presumption that he is entitled to exploit his theories. My mind recalls an instance related by a prominent lawyer, where the "whole construction of a railroad was shown to be wrong from beginning to end by the testimony of a man who had been a section foreman until he had reached a point of inefficiency even for that job."

I have known expert surgeons to be totally discredited by glib and voluble doctors whom no intelligent man would trust to sew up a cut finger.

Average professional knowledge does not supply proper qualifications in all cases; yet average doctors often testify without any investigation or experimentation, in cases involving chemical or microscopical examination. I have, on more than one occasion, witnessed the spectacle of an ordinary doctor who never saw the defendant until the day of trial, and then only for a few minutes when the prisoner knew he was being watched, setting up his opinion with an air of greatest confidence, against the experienced alienist who had been observing by night and by day without knowledge or suspicion on the part of the prisoner.

Again, it is not uncommon to see the old successful practi-

tioner, with presumptuous pride, relying entirely upon his learning—his reputation—without making the least investigation of the precise matter in dispute, in face of the well recognized fact that "experiment and discovery are so constantly changing theories on scientific subjects that the books of last year may contain something which this year everybody rejects as absurd," and when such an experiment is made by another, discovers the error of his position.

And often when the expert is well qualified, the lack of knowledge of examining counsel deprives court and jury of the expert's science.

The more counsel knows of the science under investigation the more easily can the whole truth be extracted from the scientist. It is not always easy, under our rules, for an expert, however skilled and unbiased, to state the whole truth clearly in answer to questions propounded by uninformed lawyers, and if the expert, perceiving the lawyer's lack of information, and noting the defects in his questions, suggests the needed elements to elicit the whole truth, he is called down by the other side for volunteering, and required to confine his answers to the senseless questions propounded.

Ofttimes an illustration designed to bring out the whole truth plainly, is spoiled by confusing interruptions of the examining counsel, or technical objections of his opponent. Often on cross-examination a paragraph from some book is read to the expert witness conflicting with the opinion he has advanced.

Now it is a well-known fact that writers on science, and especially medical science, have their various and conflicting theories which are sustained or combatted with great ingenuity. The other lawyer, and perhaps the expert himself, does not know that the theory supported by the quotation read may have been "vigorously contested or perhaps triumphantly overthrown by other authors."

Another contributing cause is the "Hypothetical Question." This judicial "Hydra" has been long tried, fairly weighed and, to the detestation of all fair-minded experts and the abhorrence of all broad-minded courts, has been found to be a useless vampire which, in practice, devours the very truth it was, in theory, designed to convey. Whatever the theory of the rule requiring it, in practice a vast majority of hypothetical questions do not, and from the nature of the case ordinarily cannot adequately and, therefore, impartially present either the actual or most probable state of the case. Se'dom is, and, assuming the fairest intention in the examining lawyer, rarely can the question be so framed as to embody a full and fair submission, or to embrace a completely comprehensive view of all the relevant facts or elements in the case. Therefore, the opinion of the expert, who has not himself heard all that was to be heard, nor seen all that was to be seen, must necessarily cover only a part of the ground and be misleading. The fact that other and new elements are injected, or brought out on cross examination, eliciting apparent modifications or qualifications of the opinion in chief, tends to develop a seeming inconsistency and to create in the mind of a juror an impression that the expert is a partisan, who in his original answer attempted to mislead the jury and who, finally contradicting himself, is unworthy of belief. This method has been aptly characterized by one writer as the "Hypotheses abomination—a lamentable method, vicious, misleading and subversive of every attempt at fairness." Concerning it and its answer, another has written: "It is perhaps the most abominable form of evidence that was ever allowed to choke the mind of a juror, or throttle his intelligence."

Another contributing cause lies in the fact that there is no limit, except the arbitrary discretion of a court, as to the number of expert witnesses a party may call, and it is rare when one party will content himself with a less number than his opponent had. This practice, besides producing a "motley collection

of conflicting opinions" leaving confusion worse confounded, tends to disgusting prolixity and entails an expense far beyond the value of any results realized.

Concerning this practice a Justice of the Supreme Court of the United States (29 How. 101) said: "Experience has shown that opposite opinions of persons professing to be experts may be obtained to any amount; and it often occurs that not only many days, but even weeks, are consumed in examinations to test the skill or knowledge of such witnesses and the correctness of their opinions, wasting the time and wearying the patience of both court and jury, and perplexing instead of elucidating the question involved in the issue."

Another member of that high court in *1 Curtis 439* said: "It is common remark that when there is any room for a difference of opinion, experts in about equal numbers will generally be found testifying on each side."

Justice Miller, one of the ablest members who ever graced that august bench, said (4 Dill 488): "My own experience, both in the local courts and in the Supreme Court of the United States, is that whenever the matter in contest involves an immense sum in value, and when the question turns mainly upon opinion of experts, there is no difficulty in introducing any amount of them on either side."

But chief above all causes, and far more disastrous in its results, is the partisanship of the experts themselves. I do not wish to be understood as intimating that experts, as a rule, are dishonest. Far from it. No class of experts have suffered so much in reputation among jurors and the public generally as medical experts, and yet to say they all, or even generally, are dishonest is to utter an infamous libel against the most unselfish profession in the world. But there are dishonest men in all professions. I am impressed with the conviction that some make a business of furnishing expert opinions to order. Sometimes in their partisan zeal to further the interest, right or wrong, of the party employing them, they will not hesitate to inject into a case, not only an immaterial, but a dishonest element. Time and again have I heard a physician, driven to the wall for an excuse for his opinion that a litigant's injuries were not the result of accident, defend his untenable position by delivering a supposed "knock out" to the effect that he had found upon the person of the party, scars which might have been (not that they probably were) caused by syphilis—thus injecting into the case a false theory or possible defense never testified to by a single witness or suggested by any inference from the pleadings.

In a certain personal injury case in this county some years ago, plaintiff's expert testified to permanent injuries; defendant's experts testified to the contrary. At one period during the trial the medical gentlemen finding themselves together in my present chamber, fell to discussing the merits of the respective theories. One of them, at the time of the highest standing in his profession, was overheard to say: "I am an expert for the plaintiff and must necessarily hold up the plaintiff's cause of action. You are an expert for the defendant, and you must necessarily testify in favor of the defendant."

The public have not forgotten an episode occurring during an inquiry about two years ago into the sanity of Harry Thaw, where a certain prominent alienist swore that Thaw had no incurable mental disease; whereupon being confronted with a report he had made before the famous trial to Thaw's counsel, to the effect that Thaw was burdened with a "hereditary malady with a sequence of aberrations that amounted to a chronic ailment," he attempted to explain his contradictory statements with the statement that these anti-trial opinions were merely a "medical brief" for the use of Thaw's counsel during the trial.

It is just such exhibitions as the foregoing by exponents of science that provoked from a learned writer the following severe arraignment of science: "If Science, for a consideration, can

be induced to prove anything which a litigant needs in order to sustain his side of the issue then Science is fairly open to the charge of venaity and perjury, rendered the more base by the disguise of natural truth in which she robes herself;" and that caused Professor Himes, a writer in the *Harvard Law Journal*, to say: "It is often surprising to see with what facility and to what extent their views can be made to correspond with the wishes or interests of the parties who call them."

This language can apply only to dishonest experts, for it is not correct to say, in all instances, that experts shape their views to correspond with the wishes of the employer. The honest expert refuses to conform his views to any interest save what he believes to be the truth. As a lawyer cannot be expected to employ an expert whose opinion is against the interest of his client, so a scientist, who finds his views happen to conform with the view of the employer, violates no rule in engaging, for a consideration, to testify his sincere opinion. But when an expert, sincerely believing in the correctness of his views, finds himself employed to defend them because they accord with the theory which his employer seeks to establish, there naturally springs in the most honest breast a zeal to prove, in this battle between contending theories, the soundness of his own opinion. And the stronger his convictions, the more natural it is—however honest and unpurchasable he may be—that he should become the earnest advocate of his theory, and, unavoidably, a zealous and loyal assistant of the attorney paying him to establish that theory. It is too much to expect an expert, who thus looks upon the contest as a battle between the true and the false, in which he is engaged to aid in the triumph of the true, to be entirely unprejudiced. He will not sit calmly and see his theory, which he believes to be the truth (and which he is paid to establish), overturned by what he believes to be the false. The greater his sincerity, the more earnest his advocacy. The experts then become the contending parties in a contest of theories. They align themselves into classes—each becoming a champion of his own class theory, and assuming the attitude of the advocate rather than that of a scientist. The expert is then truly biased. It is a purely scientific bias due to his peculiar views. It may be likened to the religious bias of the sincere and zealous minister favoring the theory of hell fire for the sinner. "Against such a bias no amount of self-restraint, nor the most sensitive conscience will fortify a man." Such a man is often an upright, learned, conscientious man, deserving and commanding the greatest respect and profoundest admiration—all of which only tend the more to confuse the jury and bewilder and perplex the court. Time will not permit citation of numerous instances of record verifying this statement.

The field of the engineer, comprising as it does questions of drainage, dyking, dams, adjustments, etc., affords a most prolific source of some most fallacious theorizing, and of some rank partisanship. As samples of the former I recall an instance where the question before the court was the feasibility of the present system or plan now happily in operation for the drainage of our White River Valley in this county. The establishment depended, by statute, upon the findings of the court of its feasibility. The farmers were hopelessly divided. Some were actively urging the system as the only means of reclaiming and utilizing that part of the valley subject to overflow; others were bitterly opposing it as a menace carrying certain destruction to the whole valley—the reclaimed as well as the unreclaimed. Engineers were aligned in support of the opposing theories. One class contended that the overflow of the valley, which occurs for a short period yearly following our chinook winds, would result in diverting and shifting the united waters of the White and Green Rivers to the channel of the proposed canal, scouring out and irreparably damaging the whole of that fine valley. The court, however, adjudged the plan to be feasi-

ble. Several miles of canal, reaching almost the entire length of the valley, were dredged. Instead of the channel below the junction of the two rivers shifting to the canal, the White River above their junction changed its course entirely from the north to the south, and now finds its outlet through the Stuck and Puyallup Rivers to the Sound forty miles to the south, while only the waters of the Green River now flow north through the original channel, of what, before the shifting, was called White River; and for years abundant crops have been produced where for ages before there existed only marshes and duck ponds.

Again I recall where a jury in my division of the Superior Court was assessing damages for the present regrade of Fifth Avenue in this city. As all know, this avenue runs along the face of the hill. The owners of property on the east or uphill side of the street were basing claims for damages on the liability of the whole hill sliding down as a result of the new and deeper cutting. Again engineers were aligned—some on behalf of the city and others on behalf of different property owners. Both sides were familiar with the character of the soil and its different substrata, and each expert became an earnest advocate of his class theory. The jury put greater credence in the opinions of the city's engineers and awarded damages on the theory that there would be no sliding. Less than three years have elapsed. The whole face of the hill has been sliding. Costly buildings have long since toppled, a mass of ruins, while a large area of the hillside is continuously shifting, requiring the constant work of teams to keep the regraded streets free from the moving earth, to the enormous damage to the city.

But a field wherein the engineer witness becomes the partisan advocate is in cases for the assessment of damages for adjustment of property to regrades, etc. All are familiar with the rule allowing damages for buildings wholly taken or partially damaged by regrades. Where there is no means for adjusting such buildings to the regrade, they, of course, are totally lost, and then the amount is easily ascertained; but where the conditions are such that the buildings or plants affected may be adjusted, the statute allows the estimated cost of making a reasonable and proper adjustment with reference to the new grade. Here is where I have seen the engineer become a real artist. There are many different ways of adjustment; but what the law requires is the most feasible and practical adjustment, all things considered, with reference to the new grade, and for the allowance of the reasonable cost thereof. It has been, and is, the practice of some owners to employ engineers to devise plans of adjustment. Many times I have noticed that the plans were presented and advocated by the engineer witnesses with the greatest earnestness and plausibility, not with a view to procuring recoupment for actual loss, but with a view to putting the property owner in a better position than he was before. Instead of being made whole for his actual loss, he was to profit off the city.

The Supreme Court of Ohio, concerning this partisan tendency of experts, says (12 Ohio 483): "Whenever they have enlisted on the side of either party or of some favorite theory, the difficulties are greatly multiplied, and however honest or renowned for professional character the witness may be, such will be the conflict of their testimony in nine cases out of ten, that it will be utterly unsafe for a jury or court to follow or adopt the conclusions of either side."

And the Supreme Court of California (40 Cal. 396) declare: "It must be painfully evident to every practitioner that these witnesses are generally but adroit advocates of the theory upon which the party calling them relies, rather than impartial experts upon whose superior judgment and learning the jury can safely rely. Even men of the highest character and integrity are apt to be prejudiced in favor of the party by whom they are employed. And as a matter of course, no expert is called until the party calling him is assured that his opinion will be favorable.

Such evidence should be received with great caution by the jury, and never allowed except upon subjects which require unusual scientific attainments or peculiar skill."

An expert is defined in 27 A. L. Reg. 3, to be: "A man who is paid a retainer to make a sworn argument."

Elliot, in his "Work of the Advocate," says of this definition: "Bitter as this definition is, it is not entirely inaccurate. Expert witnesses usually do, with swiftness and avidity, seize every opportunity offered them to put forth an argument in the form of an opinion, and such an argument is the more hurtful because of the guise it wears. As an argument and nothing more it would do little mischief, but as an apparent opinion it may do much."

"Some experts do not realize their tendency to partisanship. Others are badgered into it by unfair efforts of cross-examiners to throw doubt and obscurity upon their direct testimony. These efforts are often instigated and directed by the expert advocate for the other side."

A prominent attorney writing in the *Yale Law Journal* a couple of years past, said: "To the jury an expert is an expert—a kind of intellectual prostitute ready to sell his opinion and enlist in the service of the side that pays him."

From "Best on Evidence" I quote: "There can be no doubt that testimony is daily received in our courts as scientific evidence to which it is almost profanation to apply the term."

The Maine Supreme Court (65 Me. 74) characterizes it as the "vain babblings and oppositions of science falsely so-called when the hopes of a party depend rather on mystification than enlightenment."

The evil is of long standing, and of increasing gravity. The subject of a remedy is being discussed by various State Bar Associations, and by numerous writers in legal and scientific journals, but there is no unanimity as to any remedy. Six of the states have enacted laws on the subject, but there is no uniformity, and but little effectiveness in the laws thus far adopted. Of the proposed remedies up to date, the two apparently most favored provide: One for the appointment of expert jurors as triers of scientific issues, while the other proposes the appointment by the court of all expert witnesses; that their compensation shall be paid from the public treasury. Various details are prescribed, such as providing for the reimbursing of the public treasury by the litigants, and for preventing the experts from knowing at whose instance, or expense, they are appointed.

The first method is not new. It has been tried. It originated in the old Roman practice (Dig. Lib. XXV. Tit. 4) and was one of the modes selected by our English ancestry away back in early times, before trial by jury was much developed, for the trial of issues relating to certain classes of facts, and so strictly was the mode adhered to that we find, even in that misty age, one instance at least of a jury exclusively of *matrons de ventre inspicendo*. This mode of trying scientific causes by expert juries continued with much regularity, as a part of the English practice, during the thirteenth, fourteenth and fifteenth centuries, and even, but with waning regularity, up to the eighteenth century.

Riley's Memorials contain numerous instances of specially qualified juries called to try such issues as: Fishing nets with meshes smaller than those required by the trade; improper tanning of hides; false tapestry; improper hats and caps; false pewter vessels; false gloves; false wine; putrid victuals; malpractice by surgeons; etc., etc.

However well this mode may have worked as a system applicable to a large and densely settled population, with many branches of science either unknown or but little understood, it is sure that under the theory of jurisprudence prevailing in our American colonies and later adopted as a part of the government of our states, recognizing the common law jury

as an integral part of our system, with our sparse population and limited number of scientific exponents of any particular branch of science, this method of calling experts as jurors was found inapplicable and gave way to our present method of allowing the respective parties to call experts as witnesses before our common law jury. And whether, in this age of advanced science, and with its numerous scientific experts and our increased population, it would be practical at this time to provide for a jury of purely scientific experts on every particular branch of science is, in my opinion, very problematic, but it is certainly very questionable whether such a law would not be violently opposed as contravening the whole theory of our jurisprudence.

And it is seriously questioned whether the other proposed remedy of placing the appointment of experts exclusively in the power of the courts would not be depriving a litigant of his constitutional right to call witnesses and produce evidence material to his case. It is, however, certain that any legislation on the subject must meet the approval generally of the bar, and it is equally certain that the bar will never approve any legislation which will enable the courts to create a privileged class of experts. A practice has latterly grown up for the court, at the instance of one litigant, to appoint one or two disinterested medical experts to examine the opposing litigant. This practice has now given rise to the charge, very extensively entertained among the bar, that the experts appointed by the court are not impartial, but are endowed with a leaning one way or the other; and when it is considered that judges are not infallible, that every judge generally has his family, or some other physician in whom he has greater confidence than in some others, and which doctor, notwithstanding, may be a charlatan in the profession, or under regular salary from some interest, there is some ground for this complaint.

An attempt has been made in some states to meet this by legislation requiring the judge to make appointments from lists selected by the parties, but in practice there has been found no way to compel the parties to agree on selections. The truth is, no legislation will afford a complete remedy. Something in addition to legislation is required. The right kind of laws can, however, do some good. If I were recommending any legislation I would propose a more liberal rule or policy for the admission of expert opinions. I see no objection to the judge appointing the experts from lists selected by the parties when they agree, but in case of failure to agree, I would not deprive a litigant of the right to call, at his own expense, his expert witnesses, but I would limit the number he should call. The party thus limited will be disposed to call only the ablest experts. This makes for economy in time and reliability in quality. In all cases where a litigant expects to rely upon expert testimony he should be required to file in the case notice of such intention, stating the subject, or scientific inquiry on which he proposes to offer expert evidence. Thereupon the court should have the authority, at its discretion, to appoint two experts, skilled in the same branch of science, to be paid out of the public treasury and to sit in the court room during the trial and hear all the evidence bearing upon the subject of expert inquiry, and to be called by the court, or by either party, after examination of the parties' experts, to give their opinions and to be subjected to cross-examination by both parties. Provision can be made for recoupment.

I would not restrict counsel to the hypothetical question, but would allow the expert witnesses for both sides, and the court's experts, sufficient latitude, by way of illustration, explanation or otherwise, to enable the jury to understand and comprehend exactly, if possible, the experts' positions. When the judge or juror knows the reasons for an expert's opinions he will be better able to weigh that opinion, and the court's experts will be better able to approve or disprove the same.

Such in brief are some of the benefits we might derive from

legislation, but I venture the suggestion that no legislation will make an unlearned witness competent, or a dishonest one honest, or a biased one impartial. Something besides legislation is necessary to prevent our present practice putting its premium on perjury, or reducing the honest expert to the level of the charlatan.

The real remedy, the true reform, in the final test, rests with and must come from the persons largely responsible—the professions themselves, comprising the expert witness and the lawyers. So long as it is profitable to use or to give faked or biased expert testimony, so long as it can be bought and sold without loss of professional standing, so long will it be a commodity hawked in the trial courts.

"In nearly every city of importance," writes a thoughtful observer, "there is a doctor notorious among lawyers as 'plaintiff's expert' who can be relied upon to give plaintiff what he wants. The lawyers who use him on a contingent fee retain their standing at the bar," and I might add, on the other hand, there are in such a city one or more doctors under stated salary for employers of labor, and who are known among lawyers and jurors as "defendant's experts."

The result is that doctors have largely become known or classed as "plaintiff's experts" and "defendant's experts." One class magnifies symptoms and injuries, the other minimizes and makes them imaginary. To quote from one of the aptest writers on the subject: "The plaintiff's expert has argued and reasoned himself into a frame of mind that sees in the given case just what the plaintiff's attorney needs. On the other hand, the defendant's expert sees a maligner in every man who asks damages. It is the old story of bringing to the market what the market demands. If deformities are the fashion, deformities are cultivated. We are not talking of charlatans. The doctors who are doing this are the leaders in their profession, who qualify with respectable medical degrees, professorships in leading medical colleges, and membership in the principal medical societies. Now, as long as these men can do this and remain leaders in their profession, just so long is any chance at real reform postponed. Just as long as a leading physician can accept a general retainer from a street railway company and appear day after day, in case after case as 'defendant's expert' and retain his professional respectability, just so long will you have 'plaintiff's experts' and 'defendant's experts.'"

It is not against a physician that he is under a salary from a railroad company, but this relationship makes it unprofessional for him to act, at the same time, as expert witness. His place is beside the counsel and as a medical advocate, not witness. The doctors can so frown upon the practice of acting as medical counsel and witness as to stamp it out.

When the professions "set a moral standard that demands that a member testifying under oath in court must state his opinion fairly and fully without bias and without regard to the side that calls him, neither suppressing nor overemphasizing any aspect of the case, then and only then will you have real expert testimony."

"When you have that standard established the charlatans and fake experts will be driven from the courts, because what they have to offer can not be successfully used."

Having exposed the shortcomings of other professions, I now turn to my own, and charge the legal profession with its share of responsibility. The lawyers have done as much as the experts to create a demand for "plaintiff's experts" and "defendant's experts." If the lawyer would refuse to buy, the expert could not sell. Lawyers whom no motive would induce to suborn an ordinary witness will offer a premium for the biased expert. Attorneys who would scorn to pass counterfeit bills will not scruple to palm off fake expert testimony on a jury.

There will always be lawyers who will look upon "lawsuits as games to be played and won by any means that the rules

allow" and this seems to one of the rules of the game. If the honest expert will not give him what he demands he vigorously searches in the open market for what he wants.

"If he cannot get the real article he furnishes up the counterfeit and passes it off on the jury. If he finds that the genuine expert opinion is against him, he may, at least, deliberately play the game with the counterfeit to disgust the jury with all expert testimony and even up things by leading the jury to disregard it for both sides."

"As long as the standards of the profession countenance this abuse, so long will it continue. Whenever the good lawyers will not, the shysters cannot continue to misuse expert testimony."

I cannot resist the temptation, at this point, to relate the instance of a certain lawyer in a case in one of the eastern states, who after having introduced expert evidence and finding himself confronted with outweighing contradictory expert opinions, and realizing overwhelming defeat if reliance were to be placed upon such evidence, in addressing the jury said: "Gentlemen of the jury: There are three kinds of liars—the common liar, the d—d liar, and the scientific expert."

The legal profession can reform itself. The ambulance-chasing lawyer is becoming extinct before the frowns of the profession. The present code of legal ethics came in response to the general demand of the profession. The good sense of all the professions must adopt standards in the use of expert witnesses which will make such witnesses useful and their evidence effective in the interest of truth. If the professions will establish the standards, the court will enforce them.

A scientist in the classroom aims to teach truth, and when in the court room, where a life may depend upon his words, he should be equally as impartial. He should advance nothing before a jury he would not advance before a learned society or before a class.

An expert witness should be in practice what he is in theory—an adviser of court and jury. The judgment of a scientist based upon partial facts is as unjust as a judgment of a court similarly based. No lawyer expects a biased judgment from a court. He has no more right to expect one from an expert. The expert who is the sole repository of this scientific knowledge, the sole possessor of this peculiar skill, owes it to his position as a true scientist to declare the truth as he sees it; just as the judge possessing the knowledge of the law, owes it to his position to declare the law as he sees it. A scientific man is not a concealer of truth, but a searcher after concealed truth, and, unlike the habitues whose existence depends upon concealment, he should come into court with clean hands and a pure heart, with sincerity of purpose, with a tendency and desire to ascertain and recognize truth wherever and whenever it may be found—whether in the silent meditations of his library, or after the soul-burning and anxious experimentation of his laboratory, or whether brought out by the disputes, disagreements and discussions in the court room; to conceal nothing, ever mindful of his oath which requires him to speak, not a partial, but the whole truth; or, in the language of Dr. Walton: "His testimony should be the colorless light of science brought to bear upon the case * * * To the true expert, in that responsible position, the utterance of half truths should be simply impossible."

THE SMOKE NUISANCE; A QUESTION OF CONSERVATION¹

By RAYMOND C. BENNER AND J. J. O'CONNOR, JR.

Received March 13, 1913

INTRODUCTION

Neither for those who live in nor for those who even visit an industrial centre which burns a large quantity of bituminous coal, is a definition of the smoke nuisance necessary. Its effects

¹ An address delivered at a recent meeting of the Canadian Conservation Commission.

are apparent on every side and no man, woman or child escapes them. The smoke nuisance is truly a modern plague.

It is only within the last few years that any serious study has been given to the various phases of the problem other than to the engineering. However, a remarkable change has taken place. There is not a city in the country that has the smoke nuisance in an acute form that is not aroused to the seriousness of the problem and is not attempting in one way or another to abate it.

It is rather appropriate that the city of Pittsburgh which, with its sobriquet "The Smoky City," has long been held up as the shining example of the smoke nuisance should be the center of an investigation which claims for itself comprehensiveness of plan if no other merit. It leaves no phase of the smoke problem untouched. The donor of the fund for this investigation was actuated by the belief that a thorough investigation would reveal not only the nature, extent, and precise cause of the smoke nuisance, but also the remedies that would make its abolition possible and practicable. To carry out this investigation, he placed \$40,000 with Professor Robert Kennedy Duncan, Director of the Department of Industrial Research of the University of Pittsburgh.

In this paper we endeavor to present the various phases of the problem as they have come to our notice in our work in the smoke investigation.

THE CHEMISTRY OF SOOT

When one considers the very different conditions under which coal is burnt, it is obvious that the character of soot must vary. All conditions in the furnace greatly affect the amount of carbon lost in soot, but the fact stands out that where equal amounts of coal are consumed domestic installations are worse offenders than boiler furnaces. Loss of efficiency through the escape of soot itself is small. This is, however, an indication of a far greater loss in the shape of unburned, invisible gases, which loss may be as high as 10 per cent.

Soot consists of:

(1) Carbon in a finely divided state. This, as is well known, is lamp-black, the basis of most black paints and has a great covering power. It has the power of absorbing the corrosive acids which are produced by the combustion of coal containing sulfur.

(2) Tar. It is common coal tar which makes the soot cling tenaciously to everything with which it comes in contact. Tar contains carbolic acid and a large number of other compounds of an injurious nature.



FIG. 1—A PITTSBURGH BUILDING PARTIALLY CLEANED

(3) Acids. Sulfurous acid; sulfuric acid; hydrogen sulfide; hydrochloric acid together with a number of organic acids.

These acids corrode and tarnish all of the common metals. They attack many of the stones and building materials, especially limestones. Draperies, paper, paints and other decorative

materials suffer to no less extent. In burning the sulfur in the coal, the relatively inactive sulfurous acid is for the greater part produced, but this soon becomes oxidized in the air to the far more active and corrosive sulfuric acid. These acids are also poisonous and detrimental to health.

(4) Ash. This is the least injurious of all the constituents of smoke and may be, for all practical purposes, considered as common dirt.

(5) Ammonia is found in soot only in very small quantities and is of less importance than the other corroding agents.

(6) Arsenic. This poisonous substance has been found in small quantities (generally less than 0.1 per cent. of the soot).

The amounts of these constituents of black smoke vary between the widest possible limits, depending upon the composition of the coal, methods of firing, amount of air, temperature of the furnace, etc. The following analysis of soot taken from Cohen and Ruston's "Smoke, a Study of Town Air" gives a good general idea of what one must expect.

INDUSTRIAL SOOT—SOOT FROM BOILER FURNACE Boiler chimney

	Original coal	Boiler chimney			
		Bottom	13 feet from base	70 feet from base	Top of 110 ft. chimney
Carbon.....	69.30	19.24	16.66	21.89	27.00
Hydrogen.....	4.89	2.71	0.86	1.44	1.68
Tar.....	1.64	0.09	0.28	0.80	1.14
Ash.....	8.48	73.37	75.04	66.04	61.80

DOMESTIC SOOT

Dining room flue

Constituents	Coal	Kitchen flue	Dining room flue	
			Bottom 5 ft. from grate	Top 35 ft. from grate
Carbon.....	76.80	52.34	36.45	37.22
Hydrogen.....	4.90	3.68	3.51	3.51
Tar.....	0.88	12.46	34.87	40.38
Ash.....	1.80	17.80	5.09	4.94

THE PER CENT OF FREE ACID IN SOOT

Sources of sample	Base of chimney	Top of chimney
Brass foundry.....	0.00	0.65
Study flue.....	0.50
Kitchen flue.....	0.0
Boiler chimney.....	1.62	0.56
Fireplace.....	0.37	0.00

Dr. Russell found that the rain water did not contain acid unless it also contained soot. The amount of free acid in nine samples calculated as sulfuric acid was found to be: 1.4 per cent., 0.5 per cent., 7.2 per cent., 0.0 per cent., 4.9 per cent., 0.8 per cent., 1.2 per cent., 2.3 per cent., 0.0 per cent.

From the above analyses it is seen that the amount of tar and carbon in the soot from domestic fires is much higher than that from boiler furnaces, while in the case of ash the reverse is true. Domestic soot is thus by far the more objectionable and is produced in greater quantities from the same amount of coal. The amount of acid depends more upon the amount of sulfur in the coal than upon any one factor and is given off with the products of combustion whether smoke is produced or not. When, however, soot is produced, a large percentage of the acid is occluded in the soot, where it is more injurious than if allowed to escape alone into the air. The soot coming in contact with metal, stone, decorations, etc., is made to adhere firmly by means of its tar content, in reality covering the surface with a coat of black paint. The acid is not readily washed away by the rain, but continues to act until it is all used up. This acid absorbed from the air by the rain water would be more injurious if it did not drain off from most surfaces before its action was completed.

DETERIORATION OF BUILDINGS AND BUILDING MATERIALS

After considering the various phases of the chemical composition one can readily understand why houses in a smoky atmosphere look grimy and miserable and why the use of skylights is in many places made impossible, while in others it is necessary to so arrange them that they may be readily cleaned.

Otherwise they would soon become unsightly because of the accumulation of soot. Again, changes in design to make a different arrangement of drain pipes, etc., are, at times, necessary in order to prevent the splashing of rain water containing soot upon the building.

In a smoky city, too, much more glazed tile and vitrified brick are used for the outside of buildings, as it makes the cleaning a comparatively simple matter, washing alone being necessary. Building stones, such as limestone, marbles or sandstones with calcareous binding material are rapidly disintegrated by the acid in the soot and air. Therefore materials such as granite, sandstone (with a siliceous binding), brick, etc., which are not readily attacked by the sulfurous and sulfuric acids in the soot, should be utilized. But unfortunately, that stone which is most easily affected, disintegrated by the atmospheric acid and decolorized by soot, is the one which it is easiest to work into the desired shape for building purposes. Granite and similar stones which are practically unattacked by acid and impervious to moisture, and which are readily cleaned, are extremely expensive because of the difficulty in working. Thus the architect finds himself confronted with monetary as well as esthetic considerations. Stone may be cleaned but to say the least, it is but a temporary expedient and represents a periodical tax on the owner. The logical thing is to make cleaning unnecessary by water-proofing the stone and doing away with the smoke. The sulfuric acid acts on the calcium carbonate (the principal constituent of stones most easily corroded by the acid in the soot), forming calcium sulfate (gypsum) which is more soluble in water than the calcium carbonate but, at the same time, causes the stone to undergo a physical change, making it swell and become porous and friable and easily disintegrated, also roughening polished surfaces, thus making them more readily attacked by acid and moisture and affected by weather. Dr. Angus Smith has found mortar to contain as high as 28.33 per cent. of sulfuric acid, equivalent to 48.16 per cent. CaSO_4 , caused by the action of the sulfuric acid in the air on the calcium carbonate.

The effect of the sulfuric acid on most metals is rather marked and greater than the action of a like amount of acid in the rain water or air. It would seem from observations taken in Pittsburgh, that where soot containing acid is made to adhere to the metal by means of its tar content, an electrolytic action is set up, making corrosion much more rapid. In case of iron and aluminum, the oxide and basic sulfate are produced, at least in part, from the sulfate, and the acid is used over and over again. To experimentally verify these observations, duplicate sets of various metals were fastened to two boards. One set was protected from the soot in the air by means of cheese-cloth, yet still exposed to the air and rain. The other set was left unprotected. The pieces of metal left unprotected from the soot show a greater amount of corrosion than those which were protected. I wish, here, to call your attention to the following figures obtained by Messrs. W. B. Worthington and A. Rattray, showing the corrosive effect of the acids in the air. Quoting from Cohen, "A number of rails were placed in suitable positions by the side of the line, and weighed at intervals and the loss in weight recorded. The rails were of the ordinary railway section weighing 86 lbs. per yard. The annual loss of weight from corrosion was as follows:"

	Loss in wt. in lbs. per yd. per average year	No. of years of observations
1. In the center of the town.....	1.04	17
2. In dry place in smoky tunnel.....	1.48	13
3. In a wet place in same tunnel.....	1.71	8
4. On the seacoast among sand hills.....	0.18	17

The question of exterior and interior decoration is one affected as much by the amount of smoke in the air as by the tastes of the owners of the buildings.

Interior draperies and paper are soiled much quicker in a smoky city than elsewhere. If light paper is used in papering the rooms, it must be cleaned every six months and new paper put on every year to keep it looking only half as well as one would wish.

The acid in the soot attacks draperies, rendering them useless in a short time. The extra wear of cleaning shortens the life markedly. On interior painting the effect is not as marked because cleaning is done about every so often anyway. But the problem of interior decoration and keeping the outside of a building clean are problems, indeed, and next to an impossibility in some smoky places. The statement has been made to us by a number of painters that they have done jobs which looked really as bad after two or three days as they did before they were painted. Soot certainly destroys the esthetic value of paint very quickly. The time it takes to accomplish the pollution is, of course, dependent upon the amount of soot in the air, the color of the paint, tar in the soot, etc. The number of paintings necessitated to keep the same building as presentable as in a smoke-free city will naturally vary greatly. Cases can be cited where it is necessary to paint three or four times as often as would be required for protection. In the majority of cases in smoky cities the number of paintings required is probably doubled. Sometimes it is necessary to remove the soot and tar and to wash the building before applying the next coat of paint. This washing also removes the paint, often making necessary two coats in place of one for a proper covering. After the wood has received ten to twelve coats it is customary to burn off the paint. This is an additional expense and likewise endangers the house with fire. The action of soot on the wearing qualities of the paint also depends on many factors involving the chemical composition of the paint and soot. The soot may be acid, neutral or even slightly alkaline. Places are known where the soot is thought by some to act as a protective coating, while in others it is corrosive to the painted surface, destroying the gloss and rendering it much more easily weathered. The latter is probably true in those cases where the coal burned contains a lot of sulfur and the soot is consequently quite acid.

SMOKE AND THE WEATHER

From a preliminary study of available data and a perusal of the literature concerning the meteorological branch of our work, Dr. H. H. Kimball arrived at the conclusions:

(1) That city fogs are more persistent than country fogs, principally because of the increased density due to the smoke which accumulates in them.

(2) In consequence of the fog prevalence there are fewer hours of sunshine in the city than in the country.

(3) The sunshine is less intense than in the surrounding country, the light of short wave length of blue light suffering the greater depletion.

(4) Daylight, which often depends entirely upon diffuse daylight from the sky, is depleted by smoke in greater proportion than direct sunlight.

(5) Minimum temperatures are markedly higher in cities than in the country, in part, of course, because of city heating, but principally because the smoke acts as a blanket to prevent the escape of heat at night.

We find when using a chemical method for determining the intensity of daylight that on some days there is two or three times the light as measured by chemical action, ten miles from the center of Pittsburgh as there is in the city proper.

The amount of soot in the air varies greatly, depending upon the direction and strength of the wind, etc. We have found variations between 0.0015 to nearly 0.2000 gram per 1000 cu. ft. We have many more times the soot in the air on some dark days than we have on clear, bright days.

Visibility determinations (the distance one can see) vary

greatly from day to day. With the accumulation of more data we hope to trace a relationship between these determinations and the amount of soot in the air.

The soot fall (the amount of soot which falls on a given area in a given period of time) is of interest to us from many viewpoints. A large number of determinations have been made, and although they vary greatly in different parts of the city, those made at the same stations remain remarkably constant. The total fall varies between 720 and 2280 tons per square mile per year for the cleanest and dirtiest parts of the city, respectively. These figures represent the entire dust-fall, which is jet-black and is considered here, as elsewhere, to represent the soot-fall. Analyses are, however, being made for tar, organic and inorganic matter.

HOW VEGETATION IS AFFECTED BY SOOT

Trees, shrubs, etc., are utilized in a city as adjuncts of beauty, rather than a source of income, and as the smoke nuisance, as a rule, is prevalent only in cities of some size, its effect is not felt on the crops in the country district. Therefore, the effect of soot on vegetation would be considered more particularly a question of esthetics. Yet it makes felt its injurious action, both directly and indirectly. The smoke clouds limit the available daylight in two ways:

The amount of sunlight as well as diffuse daylight is not nearly as great in a smoky city as it normally should be.

If the amount of light cut off by the deposit of tar upon glass can be considered in any sense as a measure, the tar deposit on the leaf is by far the most important factor in light absorption.

The tarry matter contained in the soot coats the leaves and chokes the stomata. This injury is mechanical. Its destructive action does not, unfortunately, stop there. Like all other forms of finely divided carbon, soot has the power of occluding other substances. The tar, acids, etc., are all poisonous to plant growth and greatly lower the vitality, the acids in particular limiting the activity of the soil organisms, especially those of nitrification.

Cohen and Ruston find that the relative assimilations of laurel leaves in districts where the air contains different amounts of soot, etc., vary from 11.6 to 100. Crops of radishes and lettuce grown in different sections of the town show the possibility of correlation of the known atmospheric impurities with the yield of the crops. Trees automatically keep record of the presence of any inhibiting factor by the narrowing of their annual rings. In one case the cross section of a tree plainly showed evidence of the building of a smoke-producing factory near at hand.

We find that such flowers as roses, carnations, etc., will not thrive within the city limits of Pittsburgh, and that for this reason many greenhouses have been forced to move beyond this deleterious influence. Furthermore, many of our trees are injured if not entirely killed by the smoke.

SMOKE AND DISEASE

The effect of smoke on health has always been a much mooted question. At the present time in the city of Pittsburgh it has assumed a very practical form. The city has appropriated considerable money for a tuberculosis hospital and a dispute has arisen as to its location. Some contend that it should be placed outside the city limits, while others hold that more intensive work can be done if it is located in that part of the city where the disease is most prevalent. The advocates of the first location, as part of their argument, assert that the smoky atmosphere is detrimental to those suffering from the disease or at least that it retards their recovery. The weight of opinion seems to be against this view.

Dr. William Charles White, in a paper read before the Fifteenth Congress of Hygiene and Demography said: "As a result of our

clinical study we have come to the conclusion that the general death rate from tuberculosis in Pittsburgh is low, that there is nothing in the smoke content of the air which in any way stimulates the onset of tubercular process or militates against the rapidity of recovery from tuberculosis when once this disease has been contracted."

Dr. White's studies along this line, however, led him to declare that from his study of the air content of Pittsburgh and of disease that smoke has an important bearing on the pneumonia death-rate, in fact that it is nearly proportional to the soot-fall. Dr. White is in favor of a popular crusade for the prevention of pneumonia like that which has been waged against tuberculosis. Of course, in such a campaign serious attention would be given to the smoke problem.

Dr. Louis Ascher, of Königsberg, who has made an extensive study of the effect of smoke and dust on disease maintains that in Germany a smoky atmosphere is responsible for the increased mortality from lung diseases other than tuberculosis. He holds that not only is this increase taking place, but that persons who are the subjects of pulmonary tuberculosis die in smoke-

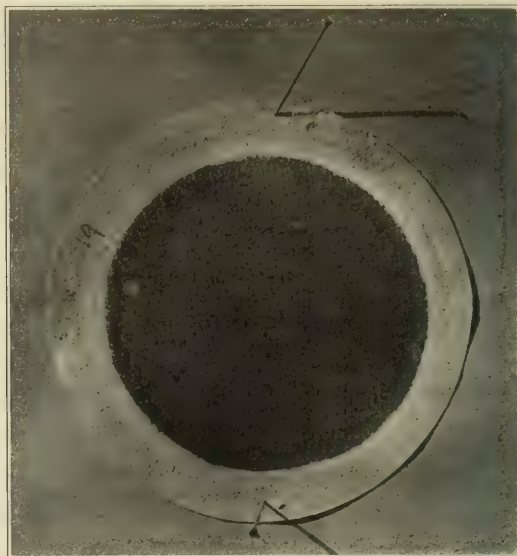


FIG. II.—FILTER PAPER THROUGH WHICH THE AMOUNT OF AIR BREATHED BY A MAN IN ONE DAY HAS BEEN FILTERED

laden districts more rapidly than those persons similarly affected, but living elsewhere.

Of the fact that carbon makes its way into the lungs of those who live in a smoky city, there is no doubt. Dr. Oskar Klotz finds large amounts of it in the lungs of Pittsburghers; 10.6 grams were found in the lungs of a street peddler 28 years of age.

According to Lehmann, while the sulfur dioxide contained in the soot is absorbed by the nasal mucous membrane, the particles of carbon are carried further into the respiratory passages. Finally reaching the lungs, they are deposited there having meanwhile in their descent given up to the bronchial mucous membrane and the lining membrane of the lungs some of the acids they retained.

Dr. W. L. Holman finds that soot acts as a disinfectant, the moist being more active than the dry. (Water seems to dissolve the disinfecting agents in the soot, making them more active.) Carbon floating in the air seldom if ever carries bacteria unless it has lodged on the ground and is again blown into the air. Soot acts as a very effective blanket, protecting the bacteria and giving them a chance to grow.

Dr. E. W. Day finds that diseases of the nose and throat are not appreciably more prevalent in smoky cities, but that they are more severe and harder to cure. This is probably due as much to the cracking of the mucous membrane by the dry atmosphere in the houses and subsequent irritation by dust as by the smoke. Singers, on visiting Pittsburgh, usually get Pittsburgh sore throat, which lasts about seven days, when they become acclimated for the time being. Unfortunately though, the same thing occurs on each succeeding visit to the city.

THE COST OF SMOKE

We are coming more and more to look at the smoke problem as fundamentally an economic problem. We have been told time and time again that smoke and soot are the products of imperfect combustion which means a waste of fuel, and a waste of fuel means an unnecessary expense. But there is more than this to the question; smoke is not only a cause of expense to the maker of it; but it is a cause of expense to every man, woman and child in the community.

Various estimates of varying degrees of accuracy have been made of the financial damage due to smoke and soot. In 1905 the Hon. F. A. Rollo Russell estimated the damage in London to be \$26,000,000. The largest single item of this amount was \$10,750,000 for extra washing and wear and tear of linens. The Cleveland Chamber of Commerce in 1909 placed the per capita loss for that city at \$12.00 or \$6,000,000 for the entire population. Mathew Nelson, Chief Smoke Inspector of Cincinnati, asserted that the loss there was \$100.00 per family. Mr. Paul Bird, in his report as Chief Smoke Inspector of Chicago, declared that the loss in Chicago was at least \$17,600,000 or \$8.00 per capita. In a paper read before the American Civic Association, Herbert M. Wilson, Chief Engineer of the United States Bureau of Mines, stated that a careful government inquiry into the toll paid by the people of the United States showed a total of over \$500,000,000 or a per capita toll of \$17.00 a year for every man, woman and child in the larger cities.

These figures startle. It is the task of those who are engaged in the economic phase of the smoke investigation to make estimates for Pittsburgh as accurate as possible by inquiring into the various items that go to make up the total. They are attempting to deal not in sweeping generalizations, but in what Mr. Wood, in speaking of the work of the Pittsburgh Survey, termed, "Piled-up actualities."

About 25 per cent. of the cleaning expense of office buildings in the city of Pittsburgh is due to smoke. When you realize that the cleaning bill of some of our office buildings is \$75,000 per year, you know well what a toll is placed on them. To cite a single item—it costs a certain building in Pittsburgh \$320.00 more a month for window cleaning than if the building were located in New York or Philadelphia. The lighting bills in office buildings are increased by half because of the conditions of the atmosphere in Pittsburgh.

The damage to goods in wholesale, retail and department stores runs up into the thousands, amounting to as much as \$30,000 a year in the case of one store. We have found that it costs from 33 per cent. to 50 per cent. more to conduct a hospital in Pittsburgh than in other cities. For instance, in the matter of extra cleaning force, one hospital could save \$3,000 a year, and another \$1,200 if the city were cleaner. You have noticed, no doubt, the number of buildings in large industrial cities that are washed down or painted once or twice a year. To one firm in Pittsburgh this means an extra expenditure of \$700.00 and in the case of another firm, of \$500.00.

Census reports on laundries show that Pittsburgh pays more than most comparable cities and that it costs the laundrymen more to do the work. These figures when compared with the report of smoky days in various cities seem to indicate that

atmospheric conditions and not custom determines, in a large measure, the per capita amount of business done.

The schedules of men who now live in Pittsburgh but who come from other cities show that they pay from one-third to a half more in Pittsburgh. They wear at least two more shirts and two more collars per week which means an extra expense, at the lowest, of \$16.00 each year. Schedules of women who have lived in other cities show that they pay \$24.00 each more a year in Pittsburgh than elsewhere. The toll paid to steam laundries alone amounts to something like \$800,000. The extra expense in labor, time and effort in home laundry work is much greater than that of steam laundries. As a minimum estimate Pittsburgh pays a toll of \$1,500,000 in laundry and home washing bills.

Dry cleaning is found necessary far more frequently in Pittsburgh than in other cities because of the atmospheric conditions. Because of this a greater supply of clothing is required and clothes wear out sooner. Moreover, Pittsburghers are limited in the selection of colors of clothing. Especially is this true of woolen goods, furs, hats, trimmings, etc. The average annual bill of a man in Pittsburgh who sends his clothes to a dry cleaner is \$18.00; a woman's bill is about \$20.00. This is half more than the man or woman would pay in a cleaner city. The total extra cost of dry cleaning in the city of Pittsburgh is about \$750,000.

In October, 1912, the Philadelphia assessors, in answer to the appeal of the property owners in the 24th and 44th wards of that city, who declared that recent sales in their vicinity were at prices far below the assessed valuation because of the smoke nuisance, reduced the assessed valuation of each from \$500 to \$2,000 on some three hundred properties. A preliminary survey of conditions in Pittsburgh showed that the same facts were here true. In some sections there has been a depreciation of fully 50 per cent. in sale price. Such property is near mills or railroads or, as is often the case, near both. Houses in such neighborhoods are very difficult to rent and in order to rent at all, there must be a reduction in the rental price of at least 20 per cent. Sometimes people rent these houses and move as soon as they become acquainted with the nuisance.

To all these losses—and there are many others—must be added the cost of the fuel wasted through imperfect combustion. In 1881, when a little less than 3,000,000 tons of coal were being used in Pittsburgh, William Metcalf, an eminent engineer and mill owner, estimated the cost of the coal that was sent, wasted, out of the tops of the stacks at \$1,063,000. At the present time Pittsburgh burns in the neighborhood of 15,000,000 tons of coal annually, the cost of which is about \$19,000,000. It has been estimated, on the basis of efficiency tests, that there is a loss of \$4,000,000 annually which could be saved by proper furnace operation.

FACTORS TO BE CONSIDERED IN THE ABATEMENT OF SMOKE

As a problem the smoke nuisance presents many and various phases. In the method of attack in the different cities there are a number of factors which must be taken into consideration.

1. The topography of the country is an important factor in the mitigation of the evil. A hilly country, such as we have in Pittsburgh, confines the smoke to the valleys, so that it is not readily carried away by the wind as it is in Chicago and other cities built on a flat country.

2. The location of the smoke-producing plants with reference to the residence district must be taken into consideration. In many places this proves a source of great annoyance, in others tends to simplify the problem. In Pittsburgh the mills are situated along the Ohio, Allegheny and Monongahela rivers, which run through the city, bounding at least three sides of our best residence districts. Recalling the topography of the city you can see that this does not facilitate abatement.

3. The necessity for burning soft coal in private dwellings is a great bane, the methods for burning it without smoke not being nearly as well perfected as in case of large installations. About 6 per cent of the coal burned in fireplaces and other domestic installations escapes through the chimney as soot,



FIG. III—A LOW STACK AMONG HIGH OFFICE BUILDINGS

while only about 0.5 per cent of that burned in power plants is thus wasted; that is, weight for weight, the coal burned in domestic installation is twelve times more a nuisance than that burned in a hotter furnace under a boiler. Cities which have at their disposal a supply of natural or other cheap gas are greatly favored.

4. Cities, such as Philadelphia, which have access to cheap hard coal, should have very little need of consideration in connection with our problem. Anthracite coal is a smokeless coal. In fact, soft coals vary greatly in the ease with which they are burned without smoke. Different types of mechanical stokers and other kinds of installations are required in many cases. Each district presents new engineering problems. An installation which gives perfect satisfaction with one kind of fuel will not of necessity do so with another.

5. Smoke abatement is not a difficult task in non-manufacturing towns where power plants are the exception rather than the rule. In manufacturing towns, on the other hand, long-continued campaigns of education are necessary before even the enforcement of an ordinance is possible.

After a thorough perusal of smoke literature and a general survey of the smoke-producing plants in this district, a number of facts were firmly imbedded in our minds:

(1) That the production of smoke was in most cases unnecessary and could be prevented with economy to the power plant operator.

(2) No thoroughly practical method is known for abating

the smoke in roundhouses, coke ovens, brick kilns and one or two special furnaces.

(3) However perfect a smoke preventing device has been installed, it will not be of much value for the prevention of smoke unless intelligently operated, *i. e.*, the fireman must be educated to do his work in a proper manner.

(4) The public in general were of the opinion that in order to be prosperous the city had to have smoke, *i. e.*, that it meant industry and prosperity.

(5) No investigation of the subject as a whole had been made by the coordinated efforts of a group of men.

We find that certain types of installation are notorious smokers while others are practically free from smoke at all times.

Furnace Type	No. of stacks observed	No. violating the city ordinance
1	45	26
2	21	3
3	8	0
4	23	15
5	15	0
6	1	0

The human element must not, however, be neglected in this connection. It is possible for a skilled fireman to operate a hand-fired furnace without objectionable smoke even if it is not constructed in the most approved manner. But given an unskilled or careless man in charge, the most modern of plants may become an objectionable smoker.

To do away with smoke and increase efficiency one must bear in mind three things:

1. The mechanical contrivance for burning the coal must be suited to the purpose.

2. The fireman must be trained to do his work in a proper manner.

3. Some method of furnace control should be employed (CO_2 recorders, pyrometers, etc.) so that the efficiency of the furnace, amount of smoke, etc., may be known both to the fireman and superintendent.



FIG. IV—HAND-FIRED AND STOKER-FIRED STACKS

THE QUESTION OF LEGAL REGULATION

As legislation follows rather slowly the agitation for and need of certain reform measures and as the question of smoke abatement in the United States is of comparatively recent date, we need not be surprised to find that the passage of ordinances on the subject, especially of ordinances that are in any way effective, has taken place in only the last ten years. This is not true, however, of England where the law took cognizance of the smoke nuisance as early as 1273, when the use of coal was prohibited in London as prejudicial to public health. There is in existence a statement that one John Doe was, in 1306, tried, condemned and executed for burning coal in the city of London. Since 1273 there have been numberless proclamations, parliamentary commissions, laws and ordinances on the smoke nuisance.

It was about thirty years ago that cities of the United States began to pass smoke ordinances. However, as early as 1856 an ordinance was introduced in the council of Cleveland to prohibit the use of soft coal in manufacturing plants, and some time prior to 1869 Pittsburgh passed an ordinance which con-

tained the provision "that no bituminous coal or wood should be used in the engine or any locomotive employed in conducting trains upon any railroad." Chicago and Cincinnati were the first cities to pass general ordinances on the subject, the first ordinance in Chicago being passed in 1881. Pittsburgh did not have an ordinance until 1891 and then it was for only a section of the city.

At the present time all of the cities having over 200,000 population, with a few exceptions—and in these cities the problem is not acute—have smoke ordinances, as have many of the smaller cities which are far-sighted enough to be on their guard, lest this modern industrial plague come upon them in its full wrath.

The source of power of governmental authority to abate the smoke nuisance is the police power of the state. We are always tempted to think of this as extending only to the protection of life and property in its narrow sense and the maintenance of public order, but more and more we are coming to know that its great sphere is public health and general welfare. This police power may be delegated by the state legislature to municipal corporations, and this is the power under which municipalities declare certain acts nuisances. While a municipality may be authorized in general terms to declare what shall constitute a nuisance, it may not declare that to be a nuisance which in fact is not. In common law "dense" smoke was not a nuisance *per se* though some courts have held it to be so in a populous city.

The Pittsburgh ordinance of 1906 was held void for two reasons, one of which was "that the Legislature of Pennsylvania had likely not given the city sufficient authority to pass an ordinance upon the subject." The city at once sought and secured the power. Thus it can be seen that in order to deal with the smoke nuisance, cities should seek specific authority from the legislature.

When a municipality is thus empowered it is then in position to pass an ordinance. It is a difficult matter to say what the



FIG. V.—A STEEL MILL—ONE OF THE WORST OFFENDERS

essential provisions of a smoke ordinance should be and yet from the experience of the different cities we are able to select certain features that are necessary if the ordinance is to accomplish any notable results.

In our day and generation we are looking to preventative rather than remedial legislation for telling achievement. This thought leads us to one of the fundamental functions of a smoke ordinance: that it should make provision for prevention as far as possible of the installation of improperly designed furnace equipment. For this purpose the ordinance should provide that plans and specifications for all construction work on furnaces be submitted to the smoke inspector and approved by him before the work is started.

This feature leads us to the point that since it is so important a provision, the ordinance should state the qualifications of the man whose duty it is to pass on these plans and specifications. Surely it should provide that he be an engineer, "qualified by technical training and experience in the theory and practice of the construction and operation of steam boilers and furnaces."

An ordinance, of course, should state the density of smoke that is to be permitted and provide a standard of measurement. On the first point, care should be taken lest the provision be somewhat vague, for this has been the rock upon which many ordinances have been wrecked in courts. In speaking of this feature—the fixing of the density—Mr. S. B. Flagg, of the United States Bureau of Mines, says: "The requirements should represent the best practice, the standard set should not be an impossible nor an impracticable one, neither should it represent ordinary or poor practice. In some ordinances a stack well within the limits as set by the ordinance may be responsible for the discharge into the atmosphere of many times as much soot as another stack which violates the ordinance."

The mere enactment of a reasonable, efficient and enforceable smoke ordinance is not enough. The ordinance must be enforced. At this point most of the cities have fallen short. Sometimes the wrong methods are used in the enforcement of the ordinance. Most of the time the methods employed are altogether too lax and feeble to secure even mediocre results. To remedy this situation there is one great weapon—public opinion. However, in order to educate, concentrate and focus public opinion, a league or union of civic and commercial organizations should be formed in each city. Such organizations seem imperative in American cities until better results are secured by way of enforcing smoke ordinances. Eternal vigilance on the part of the public is the price of a smokeless atmosphere, but to those who enjoy such a blessing the price is not a whit too high.

Enough has been said to suggest that the smoke nuisance is an economic question and that the people who are most concerned are not those who make the smoke but those who suffer because it is made. It is necessary, therefore, to educate the public as to the evils of the nuisance, that an active and intelligent public opinion may be brought to bear on those who are responsible for it. As has been pointed out, even with the smoke makers this problem is an economic one. The abolition of the smoke nuisance, therefore, unlike many other social nuisances against which outcry has been made, would result in direct and immediate gain both to the public-at-large and to those who are chiefly responsible for the nuisance itself.

DEPARTMENT OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH

THE CHEMIST AND SCIENTIFIC MANAGEMENT¹

By H. W. GILLETT

Your secretary asked me to speak to the section on some phase of what the chemical engineer gets up against in commercial work. The most interesting thing I met in commercial work was scientific management. This is a comparatively new thing in the industrial world, but I believe it has greater possibilities for our individual and national good than any industrial

¹ Paper presented before the Cornell Section of the American Chemical Society, February 25, 1913.

development since the beginning of the introduction of labor-saving machinery.

It is a scientific development in which we have for once outstripped the Germans. Perhaps it is because it is of American instead of German origin that chemists, though eminently fitted by their training to understand and make use of it, have so far been far behind the mechanical engineer in taking it up.

Popular interest in scientific management is, however, growing rapidly; the appointment of President Taft's commission on economy and efficiency, the comments of the daily press and the formation of two national societies for its advancement, testify to this. The *Saturday Evening Post* ran a series of popular articles on it last fall, and at about the same time *The Outlook* dealt quite fully with it in regard to housekeeping. The Department of Home Economics of the Cornell Agricultural College gives lectures on it, as applied to housekeeping. Vassar College is applying it in its business office, and you can hardly pick up an engineering magazine that does not record its progress. It is time for the chemist to get into the game. I am glad to see that the February *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY* has a good editorial on it.

But why, you ask, should the chemist be interested in management of any kind? Perhaps the best answer will be to call to your minds the recent recipients of the Perkin Medal,—Acheson, Hall, Frasch and Gayley. Is it not because these men had not only scientific ability, but the executive ability that can take a process out of the laboratory and make it work on a large scale, that they stand forth as the highest type of successful chemists?

Without scientific ability they would have been nowhere, but it is equally true that without executive ability they would never have won great fame and wealth. The chemist who gets the big rewards is the one who can bring to bear both scientific and executive ability, while the one with scientific ability alone may get his name mentioned in Erdmann or Berthsen.

Our industries are drawing more and more from the ranks of technically trained men for their superintendents and managers, and there are many cases where the works laboratory is the best training school for what we may call the technical type of executive and that is the coming type.

Let us, then, take for granted the chemists' interest in executive problems; in management. What is there in scientific management for him? To answer this, let us see what conditions exist that make a place in industry for what we call scientific management.

A man starts a business on a small scale and to make it a chemical industry, let us say he makes a new kind of scouring soap. At first he is his own foreman, inspector, purchasing agent, and sales agent. He sees to the ordering of material and keeps track of the stock on hand. He hires all his men himself, oversees them, works with them and keeps them occupied with work, shows them what to do and how best to do it, sees to the weighing of the batch, the firing of the kettles, the salting out, watches that the cakes are correctly made and properly wrapped. He sees that orders are filled promptly and that quality is maintained. In short, he has the whole thing in his head and is on the job all the time.

Let us say that he has a good product and it finds a ready sale. He enlarges his field of operation, builds an addition to his factory, employs more men, and has to have a foreman, and a shipping clerk. Time goes on and he has all the departments of the large, modern factory, then some fine day he finds out that the cost of production per cake of soap instead of going down, as it should because of large production, is standing still or increasing, while raw materials are going up and selling price, through competition, is going down.

He studies the situation, or calls in an efficiency engineer to do it for him, and finds that the plant is held up because the stock of alkali has run low because the foreman neglected to

notify the purchasing department that it was needed, he finds that the new men hired in the expansion period have not been taught to work as well as the old ones he taught himself, that the men are not making any more cakes with new machinery than they did with that of obsolete design, that packing boxes have not been provided and orders for which customers are calling cannot be shipped. Probably he finds that only one man knows how to salt out the soap, and he's "off on a tear," so things are hung up again.

In short, the business has grown too large for one man to control all the details, and his organization cannot cope with the situation as he himself used to handle it when the shop was small. When an emergency arose, he had said to the superintendent: "You must get Smith and Jones' order for 50,000 cakes of Bonolio out this week." The superintendent passed the word to the foreman, the foreman told the kettle man and he put it up to his helper. Instead of planning and directing the work in detail, the older or "military" type of management tends to put the responsibility on the workmen themselves, the part of the organization least fitted to handle it.

To cope with such a situation, whether in making soap, laying brick, running a machine shop, making ladies' suits, or any industry whatsoever, there are certain principles and methods, which we call "scientific management."

It is the aim of scientific management to provide means for running the plant with the same thoroughness, planning and attention to details that the old boss used in the small shop.

Let me give you a few definitions of Scientific Management.¹

"The art of management has been defined 'as knowing exactly what you want men to do and then seeing that they do it in the best and cheapest way'; also, 'the principal object of management should be to secure the maximum prosperity for the employer coupled with the maximum prosperity of each employee.'"

Mr. K. H. Hathaway says:

"For its objects Scientific Management has the saving of energy, materials, and time, or in other words, the elimination of waste, and the increase of the world's wealth resulting from greater productivity of men and machinery. These it aims to achieve, in each industry to which it is applied, through bringing to bear upon each problem the analytical methods of investigation employed in the sciences; developing a science with well defined and codified laws, in place of uncertain tradition and rule-of-thumb opinion. This is a broad statement of the first principle of Scientific Management."

Theodore Roosevelt says:

"Scientific Management is the application of the conservation principle to production.... the time, health and vitality of our people are as well worth conserving, at least, as our forests, minerals, and lands. And Scientific Management seems to do even more for the workman than for raw materials. It studies him at his task. Of the motions he makes and the efforts he puts forth, it determines by patient observation, which are the ones that get the result. It experiments to see whether these cannot be further shortened, or made easier for him.

"When the right way has been worked out in every detail, Scientific Management sets it up as a standard for that job, then instructs or trains the workman until he can accomplish this standard, and so on, with all other workmen and all other jobs. The individual is first made efficient, his productive capacity is raised 25 per cent or 50 per cent, sometimes doubled. From these efficient units is built up an efficiency organization. And when we get efficiency in all our industries and commercial ventures, national efficiency will be a fact."

Mr. Brandeis says: "In Scientific Management nothing is left to chance. All is carefully planned in advance. Every operation is to be performed according to a predetermined schedule under definite instructions, and the execution under the plan is super-

¹ Gilbreth, "Primer of Scientific Management," pp. 1-3

vised at every point. Errors are prevented instead of being corrected. The terrible waste of delays and accidents is avoided. Calculation is substituted for guess; demonstration for opinion."

I quote also from the editorial in the February number of THIS JOURNAL.

"Modern industry was brought about by the change from handicraft to manufacture, and early British economists held that the application of the principle of *division of labor* was the basis of manufacture.

"It appears, however, that another principle is the basic one in the rise of industry. It is the *transference of skill*. The transference of skill from the inventor or designer to the power-driven mechanism brought about the industrial revolution from handicraft to manufacture. . . . Except in rare instances, no effort was made to transfer the skill of the management to the production department and to the employees, or to undertake the division of executive thought. Very little consideration was given to the workmen as a producing unit. . . .

"Another tendency has as its object the improvement of the personal relations between the employees themselves and between the employee and the employer. It is the effort to establish the best of factory working conditions, to develop and maintain a shop atmosphere free from all harassing and hindering influences. It is an attempt to make use of the results of experimental psychology in improving working conditions.

"But the most important change and one that comprehends the others, is in the mental attitude toward the problems of production. The tendency is toward an attitude of questioning, of research, of careful investigation of everything affecting the problems in hand, of seeking for exact knowledge and then shaping action on the discovered facts. It has developed the use of time study and motion study as instruments for investigation and the planning department as an agency to put into practice the conclusions drawn from the results of research, and methods of wage payment which stimulate coöperation. . . . The skill of the management is consciously transferred to all of the operations of the factory—the prominent element in present-day industrial management is through the mental attitude that consciously applies the transference of skill to all the activities of industry.

"Here emphasis is placed upon the word *all*, for the restricted application of this principle to machines and tools has been highly developed for a long period."

I have gone thus briefly into the situation that creates a need for scientific management, and into its definition, to try to indicate to those of you who are not yet familiar with industrial plants, the reason for its importance at the present day.

Now let us briefly consider the mechanism of scientific management, labor-saving devices, or, we might call it, *Quantitative Management*.

It includes:

- | | |
|---|---|
| (1) Standardized conditions and methods | } Scientifically planning
your work. |
| (2) Standardized operations | |
| (3) Planning | |
| (4) Instruction | } Scientifically working
your plan. |
| (5) Inspection | |
| (6) Efficiency reward | |

First of all we must have standardized conditions, that is, find out the best way to do a thing. This involves studying the passage of material through the shop and routing its passage so that it goes in a straight line from one operation to another without doubling on its path. It involves balancing the equipment, the floor space and the number of workers, so that every man and every machine is busy all the time without being held up by the failure of some previous man or machine to do its part.

This brings up the very important point of *dependent sequence*. Take the big generator that supplies current for our electric furnace work here. The 2200 volt induction motor has an effi-

ciency of 90 per cent. The generator run by this has an efficiency of 85 per cent. The efficiency of the set is then 90×85 or 76.5 per cent. The same principle applies in manufacture. If the efficiency of each of five operations is 90 per cent, the over-all efficiency is only 59 per cent. So we see the importance of getting *each* detail right.

Standardized conditions may involve such factors as the use of high-speed steel and the consequent higher speed of feed and greater depth of cut that are revolutionizing machine-shop practice. It is interesting to note that the discovery of high-speed steel by Taylor and White was a chemical by-product of Dr. Taylor's research work on standardizing machine shop conditions, when he was first working out scientific management. Factory machinery, dictaphones, adding machines, and improved labor-saving and "system" devices, shop forms and operation symbols¹ are often shown to be worth while, but these improvements are not the vital part of scientific management. Those who consider that improved machinery is a synonym for scientific management mistake the part for the whole. As was pointed out in the editorial already referred to, machinery has been highly developed for a long time. In fact most plants are overmachined rather than undermachined, and the aim of the organizer, or efficiency engineer, is first to secure the best use of the present equipment, keeping down the investment in new machinery to a minimum, and confining it to cases where the outlay is really imperative. Too many managers have installed expensive automatic machinery in order to halve the production cost per piece, only to find that in a couple of hours per week it would provide all the pieces used in the whole week, and that in interest and overhead charges it was eating its head off, costing in the long run more than the old way. The balance of the factory had not been taken into consideration. Such an investment is not scientifically planned.

In the standardization of raw materials, buying on specifications, and the standardization of the product, the chemist and metallurgist are called in. As an example, in one paper mill where one chemist was formerly employed, they found it necessary to hire seven as soon as scientific management was started.

As an example of standardization, consider the blueprints used in a scientifically run shop. Every dimension shows the "tolerance," or limits between which the piece will serve. Where the length of a shaft can vary $\frac{1}{2}$ inch either way, the worker does not spend time trying to get it down to $\frac{1}{100}$ of an inch. Where it must be within $\frac{1}{1000}$ in diameter he knows it and does not measure it with rough calipers and get it off $\frac{1}{100}$ of an inch or more, thus spoiling it.

Standardization also comes in in scientific hiring—fitting the man to the job. Failure on the part of a worker to attain high efficiency, if the man makes an honest effort, is looked upon, not as incompetence, but as due to bad placing or to bad instruction, both of which are functions of the management, not of the man.

Standardizing methods involves recording them. For instance, instead of the old workman who could harden steel because long practice had trained his eye to tell temperature roughly, and whose death, disability or absence threw the tool-room into chaos, we have a little slip attached to each lot of tool steel, giving the temperature and length of time required to harden that lot; thus, with the aid of a pyrometer an unskilled man can do even better work than the old skilled workman. After a difficult job in the foundry has had the proper pouring temperature and proper gating worked out, and the job finished, a card filed with the pattern tells just how best results were obtained. Then six months after, when the pattern again goes in the sand, instead of relying on the overtaxed memory of a

¹ Parkhurst, "Applied Methods of Scientific Management," p. 10. "The Science of Management in Practice," *Industrial Engineering*, Mar., 1912, p. 187; April, 1912, p. 272; May, 1912, p. 365.

foreman, or failing that, working the whole problem out again we can start where we left off. This is a part of what is meant by "transference of skill."

After our conditions are made right, we can go on to the next step, standardizing operations. Under this system all the head-work is done by the management, the workers follow instructions. Before we can issue instructions, we must be sure that we know what to do and the best way to do it.

The first thing in deciding what a man is to do is to know to whom that man is responsible; organization charts are hung in conspicuous places throughout the shop to show graphically the relation of each man to the whole organization. An organization record, accessible to all, gives the duties of each man down to the rank and file of workers, who know to what gang bosses and foreman they are responsible.

The instructions vary in their nature, from rather general ones in cases where the nature of the work involves initiative, through fairly detailed ones to workers such as shipping clerks and janitors whose work is of the same general daily nature but not absolutely repetition work, down to the detailed instruction sheets issued for the guidance of the workers on repetition work in the factory itself. I have here for your inspection samples of all three kinds (see p. 600), the first being the instructions I worked under at a foundry using scientific management, taken from the organization record, the second taken from an instruction sheet for a machine operation, and the third a part of the janitor's instructions in another plant.

The second shows the exact time for each detail or sub-operation in a whole job, divided into those that have to be done only once for the whole lot (such as studying the blueprint) and those for each piece.

I have chosen a short one here, but often a seemingly simple job may involve hundreds of sub-operations. The way the expert in scientific management divides labor into its elements and studies the interrelation of each variable constantly reminds me of the classical work of Harcourt and Essén on the reaction of permanganate and oxalic acid. It seems to me that the mechanism of scientific management is very analogous to quantitative analysis and to the methods of physical chemistry, and that the chemist should therefore grasp the principles of this new science even more rapidly than the mechanical engineer.

The janitor's instructions show a rest period included as a part of regular work. This is from Parkhurst's book on "Applied Methods of Scientific Management" (p. 301). When this came out skeptics jeered at the idea of instructions for a janitor. As a matter of fact, standardizing this work saves 20 cents per hour each day the shop runs.

The time study by which these standard times, on which these instructions are based, are obtained, is the mainspring of the whole mechanism of scientific management. A man skilled at his work and willing to cooperate with the management is chosen, and taught how to do the particular piece of work we are studying. One is chosen who is suited to the job, and he is timed, with his consent, when working at his best average gait, not on a spurt. He is paid extra for "working under the watch." Concealed stop-watch work is rarely or never justified. Tact must be used in choosing the man and explaining to him the object of the work, when time study is first started. After time study and bonus pay become well started in the shop, there is no trouble, the men often asking that jobs not yet put on bonus be studied by the watch and put on bonus pay, so that they can share in the benefit they see coming to their fellow-workers who are already on standardized, bonus jobs.

Each sub-operation is noted and timed. For instance, in filtering a dozen samples of iron ore from silica, after getting standard conditions, such as weight of sample, volume of acid used, temperature of wash water, standard angle of funnel, standard length of stem, standard filter paper, etc.; folding the

filter, picking up the funnel, placing the filter into the funnel, wetting filter from wash bottle, filling funnel with solution, each operation of washing, etc., etc., would be timed. In this case one would take just enough samples so that the solution in the first filter had run through by the time the solution had been poured into the last, and would use a wash bottle of such size that washing this number of samples could be finished without having to refill the wash bottle. Many of these sub-operations are standard. Folding the filter for filtering a gelatinous precipitate would take the same time as for the silica, though other sub-operations would take different times. After making time studies on a lot of filtrations of various materials, one could analyze the filtration of a new one into its elements. Most of these would already be standard, and a short study would give the other sub-operations so that we could readily get out standard time.

The time-study man is really making a labor assay, as it is often called, and one noted authority says that a chemist makes the best time-study man.

Time studies are usually made to hundredths of a minute with a decimal stop watch and recorded on a standard form. Often a seemingly simple operation will contain hundreds of sub-operations, and duplicate observations are made on different men. Twenty observations of each element on five different men, or a hundred observations in all on each sub-operation is the usual minimum. As the time study progresses, it is easy to see where false motions are being made, and methods of eliminating them are devised. When the false notions and the waits are cut out, we find that, in general, an operation can easily be done in about one-third the time the man does it when left to himself or merely hounded on by the foreman. This is true in almost any industry or operation you wish to name. It has been found that $\frac{1}{100}$ of a minute is not close enough for some time studies, so that very recently a scheme for getting it down to $\frac{1}{50}$ of a second has been devised. A dial a foot and a half in diameter with a hand making a revolution every 6 seconds, electrically driven, and graduated in its circumference to correspond with fifteenths of a second is set up beside the workman and motion pictures taken of the operation and of the dial. These can then be run slowly on the screen, and studied at leisure. Finally the films involving waste motions may be cut out, and the revised film used as a method of instruction to new workmen.

When this point is reached in the discussion of scientific management, the question is always asked "Doesn't time and motion study make the workman into a mere automaton, and destroy his initiative?" The most convincing answer to this is to take the questioner through a plant working under these principles and let him talk to the men on the subject. We have not time to go into this now, but I refer you to pages 49-56 of Gilbreth's "Primer." One point should, however, be brought up:

"The employee is provided the incentive of promotion. If his work could not be quickly turned over to another without fear of demoralizing or at least crippling temporarily the organization, he might be denied such an opportunity of promotion. There are many men to-day experiencing just this injustice because they have become necessary parts of a business machine which cannot be disabled even for the short time required to replace a perfectly good part by one which may need some adjustment."¹

Gilbreth is making a life-work of time and motion study. He is now working on hospital practice. The results of his investigations enable him to declare, among other things, that scientific management applied within the time-limit of actual surgical operations will cut down the ether-minutes of a patient

¹ Parkhurst, "The Science of Management in Practice," *Ind. Eng. Mar.*, 1912, p. 189.

from ten to thirty per cent. What this means in terms of lives is apparent. And even in other lines "to save time is to lengthen life."

Time study can be applied to anything. For example, one of our colleges has tried to get Mr. Gilbreth to apply it to their football formations, so that they can get by actual *measurement* the most expeditious and satisfactory method of passing the ball.¹

When the time study is complete, the time needed for each operation and sub-operation is noted opposite them on an instruction sheet which goes to the workman as a guide. About 90 per cent of this maximum speed forms the standard time, or as it is often called, "the task." The 10 per cent deduction, more or less, is made in order not to drive the man too hard, but to allow proper rest periods to prevent fatigue. In many cases, the instructions show when, and for how long, rest periods shall be taken. Psychology is drawn upon heavily for data on the science of fatigue, for use in this connection. The influence of temperature, humidity, lighting, ventilation and general sanitation on the efficiency of the worker is studied, with the invariable result that the worker gets better conditions and in turn makes more money for his employer through added efficiency.

Now we have standardized both conditions and operations and are ready to consider planning.

Under scientific management all production orders pass through the planning department, from which the order-of-work clerk allots the work to each machine, or man. The relative importance of different pieces of work is decided upon, the work of the different departments is kept in proper balance, and the records of the work in hand and the schedule of the work ahead shows whether men are to be hired or laid off, whether the sales force is to be notified that the factory is working up to capacity and cannot work on new orders till a certain time, or whether it is not up to capacity in a certain line, and that orders for that product should be gunned for.

A planning board is provided with two pockets for each work bench or machine, in one of which are next-work order cards indicating the work ahead of that bench or machine, in proper order. In each department of the shop is a duplicate of that particular section of the board, which controls that department. Duplicate job order cards are in this in order, and as fast as the jobs are completed, these cards are placed in the other pocket from which they are taken by the "move material" boss, who finds on them his instructions as to where the material on which one operation is finished, is to go for the next. When he has moved it, the card is placed in the other pocket, and is taken back to the planning room by the factory mail boy who makes his rounds every fifteen minutes. Hence the planning department knows within 15 to 30 minutes the exact state of every piece of work in the shop.

It is up to the planning department to see that orders are issued to the stock room for the proper materials for these jobs and that everything is in readiness for the job to start at the scheduled time. It issues the proper drawings, instruction sheets and bonus sheets with these next-work orders.

When there is no work for a bench, or a machine, a red card is put in that pocket, and the red areas show vividly where there is overhead expense and no production, and act as a guide to the sales force.

The planning department would be called "non-productive labor" by many old school managers, but it is merely doing in a large plant the sort of head-work that was done in our one-man-controlled soap factory. Under scientific management, instead of only one foreman trying to oversee 50 or 100 men, we have numerous "gang bosses," each overseeing a half dozen or a dozen men working together on the same sort of work.

He gives instructions showing how to cut out waste motion and how to keep up to the standard time. The men are not given standard instructions and then thrown on their own resources, but are constantly shown how to work. The gang bosses are paid a bonus based on the bonus earned by the men under them, and a still larger bonus if *each* man under them earns his bonus, so that they do not neglect any man through personal dislike. The men do not "grow into" the business, Topsy-fashion, in a hit-or-miss way.

Under scientific management, instead of making an error in the first operation on a piece and not finding it till the whole thing is finished, when all the work is wasted, we have inspection at every point, so the same mistake is not made on a second piece or second lot. Under inspection, also, we shall class cost and production records, for they constitute an inspection of the management. Proper records under scientific management have been defined as "immediate and adequate," or still better, they are to work like an "instrument of precision," accurately and without lag, *i. e.*, they must reflect wrong conditions and deviations from the standard before it is too late to remedy them. Records again, while essential, are not Scientific Management, but merely a part of a larger whole. Emphasis should be laid on this, as there are too many half-baked accountants, who, seeing the interest in scientific management, advertise themselves as "efficiency engineers," delude the board of directors into hiring them, put in a cumbersome system of forms and records, collect their fee, and leave the plant in worse chaos than before. The accountant, while useful, bears about the same relation to the real organizing engineer as the mere analyst does to the chemist.

Now the efficiency reward. If no incentive be given for the workers to go at the pace the time study has shown is proper, and we merely try to drive the men, all the work of standardizing conditions and operations is wasted. This is not the time nor place to discuss methods of pay in general, nor of different schemes for rewarding the man for doing the task as instructed and in the proper time. Suffice it to say that the best scheme is the differential bonus,¹ by which the man receives his flat day rate no matter what happens, as long as he is considered good enough to keep on the working force, and in addition, a small bonus when he begins to approximate a fair day's work, the bonus increasing steadily with increased output till, when he reaches the output fixed as the standard task or full day's work, he gets a bonus of from 25 per cent to 100 per cent of his day rate, the percentage being greatest with the work that is physically hardest, such as working over hot furnaces, for there the incentive has to be greater.

Straight piece work rates have no place in the scheme of Scientific Management.² The bonus is always paid in a separate envelope from the day rate to emphasize the fact that the added wage is paid, not for time spent, but for doing things right and as directed.

Now for some of the results obtained by scientific management. I am going to cite cases merely from the plants I have myself seen, using the new management. I visited one plant in which I picked out at random from their perpetual inventory, cards showing the cost of production of stock parts for some three years of old line management and some five of scientific management. They showed in no case less than 50 per cent reduction in cost, and in some 400 per cent.

The foundry with which I was recently connected had some dozen plants. One plant, the most modern of the lot, had always been at the bottom of the list on cost of production, though several men well skilled in the trade had unsuccessfully tried to improve its operation. An expert in scientific management who was not an expert in this particular trade, took hold

¹ Nock, "Efficiency and the Highbrow," *American Mag.*, Mar., 1913, p. 50.

¹ Parkhurst, "Applied Methods of Scientific Management," pp. 166-180.

² See Gantt, "Work, Wages and Profits."

of it, and in six months that plant was at the head of the list instead of at the foot, and the costs were less than what they had previously been. And this with no other change than the use of the principles of scientific management. And at that, they have hardly gotten started on it. A few weeks ago I saw their "lost ground" chart, on which the jobs that did not show improvement over past conditions, either in cost of production or rate of production, were marked in red. Out of some fifty jobs on which they have time studies and installed bonus pay, as I said, they are hardly started, *one* cost and *one* rate were in red, and there were special reasons which fully explained these. The rest showed improvement of 25 per cent to 400 per cent.

Still later reports from this plant show that 115 operations are now on bonus, which show an average increase in production over that under former methods of 122 per cent, an average cost reduction of 31 per cent, an average decrease in defective castings from all causes of 40 per cent and an average wage increase, in bonus, of 26.3 per cent.

Take some specific instances:

A pile of waste sand had to be taken away to allow excavating for a new building. The best bid any contractor would make for the work was \$450.00. A little time-study and the establishment of proper methods and bonus pay allowed the plant to do it for \$162.00.

Take the job on which this bonus chart was issued:

BONUS CHART 32
10/17/12

Differential Bonus for molding gang on Four Cylinder Crank Case No. ——. The following prices will be paid as *bonus* in addition to hourly wages for time consumed on the job based on good castings. Losses not due to the molding gang will not be deducted. These prices will not be lowered no matter how long the job may run from this pattern and equipment.

Cope and drag rammed in floor; 1 molder; 3 helpers

Good castings	Bonus per casting	Bonus each molder	Bonus each helper
25	\$0.020	\$0.50	\$0.38
26	0.023	0.60	0.45
27	0.026	0.70	0.52
28	0.029	0.81	0.61
29	0.032	0.93	0.70
30	0.035	1.05	0.79
31	0.038	1.18	0.89
32	0.041	1.31	0.98
33	0.044	1.45	1.09
34	0.047	1.60	1.20
35	0.050	1.75	1.31

THE COMPANY

This is a bonus chart for the molding of the crank case that goes in a well-known automobile. Note particularly the statement in black and white that these prices will not be cut.

Under old methods the average number of good castings per day was 18.2, the labor cost per piece was 59 cents. The molder got \$3.25 and each helper \$2.50, making the labor cost per piece 59 cents. Under instruction and bonus the average is 33.3 castings per day. The molder gets \$4.75 and each helper \$3.63, the labor cost per piece being 47 cents, or a 20 per cent decrease in labor cost, a 45 per cent increase in wages and 83 per cent increase in production.

The firm not only makes a bigger profit, but makes it on many more pieces, so that the cost of the time study, the inspection and the planning is repaid many fold. As to the workman, well, you're not going to have much labor trouble with your men getting 45 per cent more than the regular day rate for their class of labor. As to the consumer, he is getting castings nearly twice as fast as he was before (and he wants all he can get) without supplying more than one pattern, and that pattern cost about \$600, where under the old conditions he would have had to supply two to get the castings he wants.

Take a case in coremaking at this foundry. This job had been

run under day work from 75 to 85 cores a day, and in the judgment of the foreman 90 cores could be made in nine hours. A time study on this job was made, and the result was that the job figured 0.83 minute per core and making an allowance of about 10 per cent, the maximum bonus production was figured on a basis of 0.9 minute per core. This means a production of 600 cores per day for one man at the bench. Bonus was started at 70 per cent of this production (420) and the chart above referred to was issued on this basis. It is a pretty radical proposition to take a 75 to 90 a day job, based on the best judgment of the man in charge of that department and attempt to jump it to 420 before the men earn any extra remuneration. The man who had been working on this job refused to work under bonus and walked out. A strange man was put on the job and for the first day's work made 460 cores and the second day 537, and since that time has continually averaged very close to the 600 mark. This example is recorded here as a good illustration of the apparent radicalism of some of the results under new methods.

Here is still another example:

MEMO OF A MOLDING JOB UNDER DIFFERENTIAL BONUS

Aluminum crank case weighing 79 pounds
4 duplicate sets of equipment—38 days' run

Pat. No.	Av. good No. per 9 hr. days	Mold- ers day good	Daily wage	Wage bonus	Molding cost per good case
1	37.72	27.55	28.6	\$23.27	\$ 9.121 1.175
2(a)	36.31	31.40	32.2	25.64	12.926 1.228
3	37.64	27.70	29.1	23.06	9.607 1.180
5	36.77	26.75	28.3	24.06	8.832 1.230

Averages of four patterns... 28.35 29.55 \$24.005 \$10.121 1.203

(a) Gang on pattern No. 2 was a picked gang considered the fastest and best workers in the shop; they always worked together and received extra high wages, owing to their efficiency.

NOTE:

Old average good production under combination of day and premium... 15.15 cases

Old average good production cost under combination of day and premium... \$1.196 per case

Bonus average production increase... 87.2 per cent

Bonus average cost increase... \$0.007 per case
Old foundry defective from all causes when netting 15.15 good cases per day was 25 per cent.

Foundry defective from all causes under intense bonus production when netting 28.35 cases per day was 9.72 per cent.

Foundry defective loss under intense bonus production and Scientific Management methods was reduced 60.7 per cent.

Average bonus equals 42.2 per cent over regular day wages.

This shows an increased molding cost of nine one-hundredths of a cent a pound, but the cost of the material and labor used in melting and handling the metal and in making the cores lost in the greater number of defective castings obtained before, throws the cost balance far on the side of the new methods, even disregarding for the moment the increased profits and decreased overhead due to the large increase in production.

In another plant that I have visited, they were machining 10 pieces of a certain sort per day. Large demand for that product made it necessary to get some work done outside. The best they could get an outside firm to do was 2 per day, so the firm sent its own men and applied its own methods to the outside shop, and got 8 per day in a strange shop on an antiquated lathe.

Now for the workman's point of view. Where scientific management has been installed, the hours have been decreased and the pay largely increased. Our foundry went from 10 to 9 hours, and the production increased. I asked an old workman in one plant I visited whether he would be willing to go back to the old methods. He said "No, Sir! We do more work, but things are fixed so we can do it easier, and we get more pay."

I always tried to do a day's work for a day's pay, but what I like about this shop now is that there are no loafers who get the same pay I do and don't do half as much."

Following is a partial list¹ of the industries in which some form of labor-saving management has been installed:

Bookbinding	Machine tools	Food products
Building construction	Molding machines	Furniture
Carriage and wagon-building	Pumps	Flour
Chains	Pneumatic tools	Glass
Hardware	Sewing machines	Lumber products
Tanks	Typewriters	Pianos
Construction and repair of vessels (navy yards)	Wood-working machinery	Paper and paper pulp
Firearms and ordnance	Metal and coal mining	Rubber goods
Rifles	Metal working	Soaps
Gun carriages	Bolts and nuts	Shoes
Machinery building	Valves and pipe fittings	State products
Automobiles	Miscellaneous manufacturing	Printing and lithographing
Agricultural implements	Beer	Railroad maintenance of motive power
Coal-handling machinery	Beet sugar	Steel manufacture
Electrical machinery	Boxes (wood and paper)	Textile manufacture
Founding iron and brass	Tin cans	Woolens
General machine work	Buttons	Bleaching and dyeing
Gas engines	Clothing	Velvets
Locomotives	Cordage	
	Cottons	

This shows how universally applicable these principles are.

In fact I have been wondering how the chemical departments of our universities would strike an efficiency engineer. As university departments go, they rank well, but looked at from the point of view of efficiency, they are probably in the same class as all industries, a certain amount of work done in a difficult way, when, applying the principles of scientific management twice as much could be done in the same time, in ways easier for both student and teacher.

I know you will say: "Oh, scientific management is all right in a machine shop or a foundry, but it wouldn't do in a university—conditions there are different." That is exactly what every one says of his own business at first. It is exactly what I said at first when I was told to look into scientific management and see what was in it for our foundry. But, as I studied the question, I saw that it *was* applicable, and after the right expert was secured, it was applied with the results I have given you.

Gilbreth says, in reference to his hospital work, "A hospital is a factory, a health-and-happiness factory; and it ought to be governed by the supreme principle that governs any other factory—the principle of maximum efficiency in relation to the output."

I look at a school of chemistry as a manufacturing plant, with its product either embryo superintendents or managers of plants or else pure research men, whether employed as such in the industries or as teachers. The principles that apply to our factories will apply here.²

Parkhurst says:³

"Scientific Management applied to our public and preparatory schools, colleges and industrial and manual training schools will be the remedy for much, if not all, of the present inefficiency. . . . The greatest handicap to the remedy of this inefficiency will be the opposition of those directly involved and who are to be directly benefitted by a radical change."

F. W. Taylor says:⁴

"The illustrations chosen in this book are such as, it is believed, will especially appeal to engineers and to managers of industrial and manufacturing establishments, and also quite as much to all of the men who are working in these establishments. It is

hoped, however, that it will be clear to other readers that the same principles can be applied with equal force to all social activities: to the management of our homes, the management of our farms; the management of the business of our tradesmen, large and small; of our churches, our philanthropic institutions, our universities, and our governmental departments."

How do other university graduates who, like myself, meet Scientific Management in after life, feel about it? Let me quote again from Gilbreth:¹

"I am building a fairly large job at the present time on which I have a number of young college men, most of them from a few months to a very few years out of college. They come from the best colleges in this country, and they have formed themselves, without any suggestion from anybody, into the first Canadian Society for the Promotion of Scientific Management. . . . Now the question of academic efficiency I am not prepared to debate, but I will say this however; these young men came from different colleges, the University of Illinois, Yale, Brown, Lehigh, Massachusetts Institute of Technology, and I don't remember what other colleges, and every one of them said, 'I regret exceedingly that our professors have not taken this thing seriously, and given it to us while we were in school.'"

This year one of our largest universities has 177 working days in the college year. Allowing for Sundays and holidays, including Founders' Day, and allowing thirty days' vacation besides (though the man of college age who has to work for a living is mighty glad to get two weeks), there should be 275 working days. That gives a time efficiency of 63 per cent. Then look at the laboratories that are occupied, say 25 per cent of the time that college is in session, and you get floor-space efficiency on the line of dependent sequence, of 16 per cent. Look at the lines waiting at the stock room windows. Look into the laboratories and see the time wasted in setting up apparatus, talking things over, waiting for balances, etc., and if you get a real working efficiency of 50 per cent in any chemical department of any university, I shall be surprised.

Let us grant that producing chemists is a different sort of industry than making molding machines for example, and that the universities do not, like a manufacturing plant, get more money for giving their students more and better training, the student gets the money in the form of a more rapid and a higher rise than he would were he less well trained. Yet is there any reason why the university should not be willing to learn from any source, even though not an academic one, how to "make the best use of the present equipment?" Every one at first naturally has the idea that his industry is run as well as it possibly can be, that scientific management is something for the "other man."

We quote again from Gilbreth:²

"It's a mystery to me why the medical men take themselves for granted as the ones to manage a hospital. They seem to think that a training in a specialty is a training in management. Nothing of the kind. Management is a specialty. A doctor's training is not of the kind that would make him a manager. The surgeon is just like the old-style shop foreman, it's the instinct with him to resent suggestions from anyone outside the trade and he wouldn't work in a plant where 'non-professional' orders or instructions are tolerated. So from the standpoint of scientific management, the hospitals are back in the Dark Ages."

Does not the same thing apply to chemical schools? How many educators could qualify as up-to-date executives in a manufacturing plant? Yet are they not really forced to be executives in what is really a manufacturing plant? If our teachers of chemistry will study deeply the science of management, as they do their own science, with the thought constantly present that possibly some of the principles *might* apply to their

¹ *Industrial Engineering*, December, 1912, p. 239.

² Cf. M. L. Cooke, *Bull.* 6, Carnegie.

³ F. A. Parkhurst, "Science of Management in Practice," *Industrial Engineering*, Feb., 1912, p. 113.

⁴ Preface to "Principles of Scientific Management."

¹ Report of Dartmouth Conference of Oct., 1911, p. 358.

² *American Magazine*, March, 1913, p. 50.

work, and not solely to the other man's, there might sometime be created a scholastic environment that in turn would create in our chemical students an attitude of mind which would largely span the gulf that now exists between the college and the works in which the student is to use his college training. Why need we look back at our college days, in comparison with our work experience, as a period of hard mental endeavor, but of little actually accomplished?

It is not the hard mental work that counts in brain development, but the *efficient* work. The university deals with impressionable brains. To impress on those brains the need of planning work in advance, of setting a standard of work and then of living up to it, is vital.

I believe that a course in chemical engineering run on the lines of scientific management would teach as many chemical facts as the present courses, and might also teach a greater number of students how to think.

But whether the universities take up scientific management is not for us to decide. What each one of us *can* decide, is whether he cannot apply these principles which have brought such results in so many and so varied fields of endeavor, to his own work—to his own study in his college course, to the planning and execution of his own research work, to the lay-out and routine of his own laboratory, and to his own daily life.

If I have succeeded in awakening any interest in your minds in this new American industrial development, I shall be glad. If I have not, the fault lies with the speaker, and not with the subject.

I. INSTRUCTION FOR MANAGER OF RESEARCH DEPARTMENT

1. The Manager of the Research Department is under the direct charge of, and solely responsible to, the General Superintendent; his hours are those of the office at Plant No. 1.

2. He shall make his headquarters in the laboratory located at Plant No. 1. While he is not under the orders of any one at Plant No. 1, his location at that plant makes it advisable that he work in close harmony with the officers of that plant, since most of his observations and tests on actual foundry practice must be made at that plant. When such work is to be done, the authorization of the Superintendent of Plant No. 1 must be obtained. This is to prevent hampering the production of Plant No. 1 by the research work. In all such work no orders shall be issued to any foremen or workmen that are not fully authorized by the Superintendent's approval of the work.

3. He shall have charge of the maintenance of the laboratory, and its equipment.

4. He shall make such routine analyses and tests of materials purchased by this Company and received at any plant as shall be required by the General Superintendent.

5. He shall have charge of the pyrometer equipment at all plants and shall keep the same in working order. All new pyrometers or repair parts for them shall be ordered by the Research Department and supplied by it to the various plants on their order.

6. He shall be in general charge of all pyrometric control of core ovens, furnaces, and pouring temperatures at all the plants.

7. He shall have general charge of the preparation of specifications for the purchases of material, but such specifications must be approved by the General Superintendent and the Purchasing Agent.

8. He shall have general charge of all alloy mixtures at all plants and shall see to it that such directions are furnished the various plants as, when properly executed by the plants, will result in the alloys put out meeting the physical and chemical specifications demanded by the customer. He is thus in a general way responsible for the quality of the output at all plants.

9. He must work in close touch with the Sales Department, on the matter of customers' specifications. A customer's specifications should be O. K'd by the Manager of the Research Department before the order is booked.

10. He shall keep full and accessible records of all analyses, tests, experiments or investigations of any kind conducted by his Department.

11. He shall read the various technical and scientific journals that contain information of value to the aluminum, brass and bronze casting industry, these to be furnished for his Department at Company expense, and shall maintain a complete file of references to such information contained

therein, so as to be able to answer promptly and accurately inquiries on technical and foundry problems.

12. As opportunity offers, he should attend meetings and conventions of societies dealing with the chemical, technical, engineering and foundry problems of this business. He should make every effort to keep abreast of current scientific and technical progress in his line of work.

13. He shall collect data from the various plants, or from other sources, on foundry problems, and shall make his Department a clearing house of technical information for all the plants. When a piece of work has shown how savings can be made, or quality of output improved, this information is to be reported to all plants.

14. He shall carry on such scientific or technical investigations and researches as may seem advisable in order to solve problems that come up, or to acquire needed information. The problems may originate with him, or be suggested by the Officers of the Company, by the various plants, or by customers. Before undertaking such investigations, a statement shall be made to the General Superintendent, stating the problem, the reasons why it might be worth while to investigate it, an estimate of the time and expense attached to it, and a general outline of the methods to be used in the investigation. The work shall be undertaken only after securing the approval of the General Superintendent. In rare emergencies where problems are sent in by plants, or by other Officers than the General Superintendent, which will not admit of delay, the work may be started without waiting for his approval, but he must be at once notified of the situation.

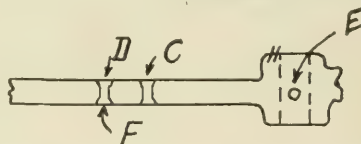
15. No analyses or tests outside of the regular routine authorized by the General Superintendent, or by these instructions, shall be made without the approval of the General Superintendent.

16. Weekly reports of the progress of the work in hand shall be made to the General Superintendent, President, and Vice-President. Copies of all letters written of any importance shall go to the General Superintendent. Where customers or sales are affected, copies shall also go to the Vice-President. Where letters concern any plant or plants in particular, copies shall also go to the Manager or Superintendent of the Plant in question, depending on the nature of the subject. In cases where the letters

II. INSTRUCTION CARD FOR A MACHINE OPERATION

NOTE
All time is expressed in Form F. A. P. 35a
Hours and Decimals
1 SHEETS, SHEET 1 DATE 5-9, 1912
ARTICLE OR JOB—PI-2-3-4-5-6 Treadles
OPERATION—DLCS

Quantity 1	Material—Iron Castings	Hand or Machine—7-D	Sketch or Drawing—10169
TOTAL	TOTAL		BONUS CHART 680
LOT TIME 0.061	PIECE TIME 0.05		
SUB			PIECE LOT
OPERATION	DETAIL INSTRUCTIONS	TOOL CUT	FEED SPEED TIME TIME
1	Preparation.....		018
2	Study drawing.....		008
3	In drill.....		002
4	Treadle from floor to table.....		001
5	On jig.....		001
6	Drill C.....	Hand	40' 006
7	Change drills.....		004
8	Drill D.....	Hand	37' 005
9	Off jig.....		001
10	Change drills.....		004
11	Drill E.....	Hand	40' 005
12	Out drill.....		003
13	In countersink.....		002
14	Change speed.....		002
15	Countersink C & D.....	Hand	70' 005
16	Treadle to floor.....		001
17	Dismantle and work order to desk		033
Carried Forward or TOTAL			040 061



WHEN MACHINE CANNOT BE RUN AS SPECIFIED, GANG BOSS MUST REPORT AT ONCE TO L. NICHOLS
INSTRUCTION 680

are of sufficient interest or importance, copies shall also go to the President.

17. Strict attention must be paid not only to the accuracy of the work done but to the promptness with which it is done and reported. In cases where there is doubt as to the relative importance of several pieces of work that call for prompt attention, special instructions shall be secured from the General Superintendent.

III. FROM JANITOR'S INSTRUCTIONS

Afternoon work, Monday to Friday inclusive

	Minutes	Hours	Bonus
17 Empty wash trough in locker room, thoroughly sweep and scrub same including floor.....	15	0.25	0.0125
18 Remove ashes (based on an average of five loads each afternoon)...	36	0.60	0.03
19 Sweep the north bay of the machine shop between the east wall and store room, and remove chips..	48	0.80	0.04
20 Sweep main press shop including erecting floor and part west of the dead line, and remove chips; includes twelve minutes rest period.....	189	3.15	0.1575
21 Prepare water in the locker room prior to the quitting whistle at 6 p. m.....	12	0.20	0.01
	300	5.00	\$0.2500

BIBLIOGRAPHY FOR INTRODUCTORY READING ON SCIENTIFIC MANAGEMENT

BOOKS

- F. W. Taylor, "Shop Management"—Harper's, 1911. Also *Trans. Am. Soc. Mech. Eng.*, **24** (1903).
- F. W. Taylor, "The Principles of Scientific Management," Harper's, 1911.
- F. A. Parkhurst, "Applied Methods of Scientific Management," *Industrial Engineering*, 1911 and 1912, Wiley and Sons, 1912.
- F. A. Parkhurst, "The Science of Management in Practice," *Industrial Engineering*, 1912 and 1913 (not in book form).
- C. E. Knoepfel, "Maximum Production, in Shop and Foundry," *Engineering Magazine*, 1911.
- H. Emerson, "Efficiency as a Basis for Operation and Wages," Pub. by *Engineering Magazine*, 1912.
- H. Emerson, "Twelve Principles of Efficiency," Pub. by *Engineering Magazine*, 1912.
- H. L. Gantt, "Work, Wages and Profits," *Engineering Magazine*, 1911.
- A. H. Church, "Production Factors," *Engineering Magazine*, 1910.
- F. B. Gilbreth, "Motion Study," Van Nostrand, 1911.
- "Concrete System," Van Nostrand, 1908.
- "Bricklaying System," Van Nostrand, 1909.
- "Field System," Van Nostrand, 1908.
- "Primer of Scientific Management," Van Nostrand, 1912.
- H. Diemer, "Factory Organization and Administration," McGraw-Hill, 1910.
- J. Hartness, "Human Factor in Works Management," McGraw-Hill, 1912.
- C. B. Going, "Methods of the Sante Fe," Van Nostrand, 1909.
- W. C. Redfield, "The New Industrial Day Century," 1912.
- J. C. Duncan, "Principles of Industrial Management," Appleton, 1911.
- H. A. Evans, "Cost-keeping and Scientific Management," McGraw-Hill, 1911.
- H. P. Gillette and R. T. Dana, "Cost-keeping and Management Engineering," M. C. Clark Pub. Co., 1909.
- J. L. Nicholson, "Factory Organization and Costs," Kohl Tech. Pub. Co., 1911.
- C. D. Hine, "Modern Organization," *Engineering Magazine*, 1912.
- L. D. Brandeis, "Scientific Management and the Railroads," Van Nostrand, 1911.
- C. V. Carpenter, "Profit-making Management," Van Nostrand, 1908.
- W. H. Tolman, "Social Engineering," McGraw-Hill, 1909.
- H. W. Dresser, "Human Efficiency," Putnam, 1912.
- H. Munsterberg, "Psychology and Industrial Efficiency," Houghton-Mifflin, 1913.
- Mrs. F. B. Gilbreth, "The Psychology of Management," *Industrial Engineering*, 1912, 1913 (not in book form).
- J. Goldwork, "Fatigue and Efficiency," N. Y. Charity Pub. Co., 1912.

MAGAZINES

Engineering Magazine, New York.
Industrial Engineering, New York.

TRANSACTIONS

Transactions American Society Mechanical Engineers.
 Transactions of the Efficiency Society.
 Transactions of the Society to Promote the Science of Management.

REPORTS

Scientific Management, Report of First Dartmouth Conference, Oct., 1911, Dartmouth College, Hanover, N. H.

M. L. Cooke, "Academic and Industrial Efficiency," Carnegie Foundation for Advancement of Teaching, *Bull.* **5**, 1910.
 Proc. Cong. Tech., 1911, "Technology and Industrial Efficiency," McGraw-Hill, 1911.

A FEW OF THE ARTICLES IN PERIODICAL LITERATURE

- W. E. Symons, "Application of Scientific Management to Railway Operations," *J. Frank. Inst.*, **173**, 1, 141, 271, 365 (1912).
- P. W. Blair, "Increasing Efficiency of a Brass Manufacturing Plant," *Metal Industry*, **11**, 13 (Jan., 1913).
- F. Crissey, "Some Efficiency Secrets," *Sat. Eve. Post*, Sept. 28, and Oct. 12, 1912; "The Self-made Efficiency Expert," *Sat. Eve. Post*, Nov. 2, 1912.
- J. H. Collins, "Figuring the Net Value of Efficiency," *Sat. Eve. Post*, March 15, 1913.
- A. J. Nock, "Efficiency and the Highbrow," *American Magazine*, March, 1913, p. 48.
- W. Lewis, "Conserving the Data of Scientific Management," *Iron Age*, Dec. 5, 1912.
- C. E. Knoepfel, "Despatching Systems in the Foundry," *Iron Age*, Dec. 5, 1912.
- F. A. Parkhurst, "Practice vs. Theory in the Science of Management," *Proc. Soc. Prom. Engineering Education*, **20**, 12 (1912).

MORSE HALL
 ITHACA, N. Y.

THE INTERPRETATION OF U. S. P. ASSAY PROCESSES¹

By FRANK O. TAYLOR

The alkaloidal assay methods of the United States Pharmacopoeia have been plentifully criticized and volumes have been written concerning changes of greater or less importance deemed necessary by various analysts. Many entirely new methods have been suggested and improved methods finally evolved from this mass of work, for use in the next Pharmacopoeia, will doubtless be more efficient than those now employed. However much we may blame defective processes for the lack of uniform results obtained by different men in the assay of fluid extracts, tinctures, etc., I am convinced that the trouble is frequently not in the method *per se*, but in the details of applying it, or in other words, in the individual interpretation of the method as stated in the U. S. P.

Now, I am perfectly willing to concede that few, if any, assay methods are given in any fuller detail than those in the Pharmacopoeia for the estimation of alkaloids and on casual reading it would seem that the methods are so explicitly stated that even an inexperienced chemist could hardly err in carrying them out, and yet if you give the same fluid extracts to several different and equally expert chemists, you are extremely liable to get some widely different results. If placed in the hands of chemists who are not thoroughly familiar with the eccentricities of alkaloidal assays, he would be a rash prophet who would attempt to foretell the variation in results obtained. This condition of affairs is one of grave importance alike to retail pharmacist and manufacturer since, with the greatly increased attention to this work during recent years, many chemists have taken it up who have not had the opportunity of acquiring the necessary experience to confer expertness and thorough reliability. This is in no wise a reflection upon individual ability or general knowledge of chemistry and pharmacy as all who have had long experience in drug assays will agree, but is simply a chemical application of the old saying that "practice makes perfect," and this peculiarly difficult variety of assays requires a great deal of practice.

As a homely illustration, suppose the pharmacist reads the instructions for the assay of Henbane, for example, he will most probably say "Surely that is so explicit that any chemist ought to be able to get accurate results," but he would not think of taking a cook-book home to his wife, expecting her to make a

¹ Paper presented at the Milwaukee Meeting of the American Chemical Society, March, 1913.

cake exactly like that made by Mrs. Smith by following the recipe unless she was a very experienced cook and had made numerous similar cakes before.

With the existing and increasing number of legislative enactments concerning standards of strength for drugs and their preparations, any errors in assay may bring about confusion and legal complications for which there is no basis in fact. Chemists working under the authority of Federal or State Governments and those responsible to individuals or corporations are equally interested in seeing that the desired standards are maintained and that conflicting analyses do not throw discredit upon analyst or producer.

It is the purpose of this paper to direct special notice to possible misinterpretation of the U. S. P. assays and in some cases to emphasize again facts that have already been published by others, but to which little attention seems to have been paid.

The adoption of uniform methods of assay for alkaloidal and other drugs is a very necessary thing, but the standardization of these methods is a very different thing from the standardization of the operations of a machine, and the literal applications of the U. S. P. methods may often give results never contemplated by the authors of the processes. As in the meting out of real justice under the terms of a law, regard must be had for the obvious intention of its originators, so in the carrying out of these somewhat intricate directions for the estimation of alkaloids we must keep in mind the evident intention of those who devised the methods and interpret the minor details in the light of this knowledge. You will recall that the eighth revision of the Pharmacopoeia became official on September, 1905, but supplementary notes and corrections were later made which were embodied in correction sheets official from May, 1907, and a few additional notes were made official from June, 1907. Copies of the Pharmacopoeia printed subsequent to this time contained all these corrections in the text, but it is quite likely that these emendations have not everywhere received due attention.

The writer's attention was recently called to a typical example of how discrepancies in assays may occur when two different chemists failed to get anything like concordant results in the assay of the same tincture of aconite, and consideration of the details of this method of assay will show how the confusion occurred and how it might happen in other cases.

In the process as described, after evaporating 100 cc. of tincture aconite to dryness, the Pharmacopoeia provides that the residue should be dissolved in a definite amount of tenth-normal sulfuric acid and distilled water and then says: "When the extract is dissolved, filter the liquid into a separator, washing the dish, and filter with about 25 cc. of distilled water." Now, there is a certain amount of extractive matter not soluble in the acid water and it is the obvious intention that this residue, the dish and filter shall be washed entirely free of alkaloid so that no loss may occur. If the washing is carried out rapidly or carelessly, it is quite possible that some of the alkaloid will not be washed out with 25 cc. of distilled water, and the washing ought by all means be continued until the alkaloid is completely transferred to the acid solution. It is next required that the acid solution, after being made alkaline with a definite amount of ammonia, shall be shaken with successive portions of 25, 15, 10 and 10 cc. of ether, the total being 60 cc. Here again the evident purpose is to entirely remove the aconitine from the aqueous solution to the ether, but, as we will see later, this will not be accomplished by this treatment and the extraction with ether should continue until this is done, which may be demonstrated by evaporating one or two cc. of the last ethereal washing, taking up the residue with a few drops of acid water and testing for the presence of alkaloid with Mayer's reagent. Certainly the exact wording of the process does not require this, but here again it is the obvious intention that this should be done and is

authorized by the Pharmacopoeia under one of the notes of correction to the article on "Alkaloidal Assay" given at the foot of page 570 in those copies printed since June, 1907, which reads as follows: "If extraction is incomplete, the process must be repeated with additional solvent. The completion of the shaking out processes may be tested in most cases by evaporating a small portion of the solution, dissolving the residue in acidulated water and adding mercuric potassium iodide, T. S., when the absence of turbidity indicates exhaustion."

From a careful comparison of the method of applying the U. S. P. assay by the two chemists in the instance mentioned above, it seemed very probable that the difference in results was due to this incomplete extraction, and in order to demonstrate the truth of this theory, a quantity of tincture of aconite was divided into different portions and submitted to four different chemists for assay with instructions that the U. S. P. process be followed literally in every particular, and after making the assay by this means the aqueous liquid should be again shaken out with successive portions of ether until the test with Mayer's reagent indicated complete extraction. The results are shown in the table below:

Grams per 100 cc. of Tincture				
	Chem. No. 1	Chem. No. 2	Chem. No. 3	Chem. No. 4
Using 25-15-10 and 10 cc. ether for final extraction.....	0.0352 0.0352	0.0372 0.0372	0.0345 0.0333	0.0358 0.0358
Per cent of U. S. P. Standard.....	78.2%	82.6%	75.3%	79.5%
Extraction continued with 25-20-20 cc. ether.....	0.0098 0.0098	0.008 0.008	0.012 0.012	0.0084 0.0090
Per cent of U. S. P. Standard.....	21.8%	17.8%	26.6%	20.0%
Final result of assay.....	0.045 0.045	0.04522 0.04522	0.0465 0.0453	0.0444 0.0448
Per cent of U. S. P. Standard.....	100.0%	100.4%	101.9%	99.5%

It will be noted above that when the process of assay is carried out exactly as outlined in the Pharmacopoeia, using separate portions of 25, 15, 10 and 10 cc. of ether, the alkaloid extracted amounted to from 75.3 per cent to 82.7 per cent of the quantity required by the U. S. P. When the extraction was continued by the use of a further quantity of ether and the total amount of alkaloid estimated, the results were very uniform, ranging from 99.5 per cent to 101.9 per cent, which is well within the practical limit of personal variation in applying an assay process of this kind. In carrying out this work, Chemists 1 and 4 each used different volumetric solutions while Chemists 2 and 3 employed the same volumetric solution, but different from either of the others.

These experiments demonstrate conclusively that complete extraction cannot always be obtained by the use of the exact quantities of solvents specified in this assay process, and the same thing is equally true of many other of the methods laid down in the U. S. P., particularly the various mydriatic drugs and physostigma, but, as indicated in the note we have quoted above, it is the intention of the Pharmacopoeia to have such extraction complete and it is necessary, therefore, to take a common sense view of the assays and be guided accordingly.

Taking the aconite assay again as an example, the separation of the ethereal and aqueous liquids is stated as follows: "Draw off the lower layer into a flask and filter the ether solution into a beaker. Return the contents of the flask into the separator....." Now, nothing is said about rinsing out the flask with water when pouring its contents back into the separator, but as otherwise some loss would occur, the careful chemist

would unquestionably do this and be carrying out the spirit of the Pharmacopoeia in so doing. Details of manipulation such as these may appear trivial and do not have a place in the pharmacopoeial statement of the assay process as they can be covered to better advantage in a general article such as appears in the back of the Pharmacopoeia on alkaloidal assay, but they must not be overlooked in actual work.

As a specific instance of this kind, Salway (*Trans. Chem. Soc.*, 99, 2149 (1911)) states that "a representative sample of Calabar beans.....when assayed by the method of the U. S. Pharmacopoeia yielded 0.091 per cent of alkaloid. The method referred to, however, was found to give results which were much too low since the amount of physostigmine isolated when working on a large scale.....was equivalent to 0.179 per cent..... The low result of the above method of assay has been ascertained to be due to the fact that three extractions with ether (as required by the Pharmacopoeia) are quite insufficient to remove the alkaloids completely from a solution which has been rendered alkaline with sodium hydrogen carbonate."

The same remarks concerning incomplete extraction are likewise true as applied to the transfer of alkaloid from its solution in ether or chloroform to an acid aqueous liquid, as in the assay of coca, cinchona, pilocarpus and the mydriatic drugs.

Turning now to still other sources of variation, attention may be directed to the methods of shaking employed. In the various assay methods the Pharmacopoeia gives definite statements as to the length of time which the powdered drug should be shaken with the solvent used for extraction as, for example, in Belladonna leaves it says: "Shake the flask well at intervals during one hour" or, when it gives the time for shaking the immiscible solvent with the aqueous solution as further in the same assay process, the statement is made: "Shake the separator well for one minute." The continuation of the shaking in the first case beyond an hour, or by shaking at frequent intervals by hand, or continuously, in a mechanical shaker, all are intended for the purpose of completely extracting the alkaloid from the drug, or rather for producing a uniform distribution of the alkaloid in drug and solvent, which practically amounts to the same thing, and if the extraction process is not carried far enough an error may creep in here, so that it is decidedly preferable to exceed the time limit of the U. S. P., especially if the shaking is done by hand at intervals, rather than to run chances of following the instructions literally and getting a low result. Scoville (*Proc. A. Ph. A.*, 1910, p. 820) has made brief reference to this same point, and others have probably done the same thing, but additional emphasis is by no means uncalled for.

In another paper (*Proc. A. Ph. A.*, 1910, p. 874) Scoville has pointed out a very serious source of error in the assay of fluid preparations of the mydriatic drugs in that these have the very peculiar characteristic of being less easily extracted when old than when freshly made if the U. S. P. process is strictly followed. He has shown that fluid extracts of belladonna, hyoscyamus, scopolamine and stramonium, when freshly made, may usually be extracted completely by following the U. S. P. process, but after they have aged for one or two years it is impossible to extract the full amount of alkaloid present by the strict use of the U. S. P. process, and the same difficulty sometimes occurs even in freshly made extracts. The addition of a small portion of alcohol to the chloroform used for the preliminary extraction permits of the complete and much more rapid removal of the alkaloid from the aqueous liquid. It may seem that this is going beyond the bounds of the U. S. P. process, but I do not believe this is the case since in the pharmacopoeial note on the alkaloidal assay (page 579), it states that if an emulsion forms which cannot be easily broken, it is permissible to use a "slight amount of alcohol to assist in breaking this emulsion, and as emulsions are specially liable to form in the assay of the mydriatic drugs, alcohol would

very likely be used in many cases, and it is certainly not overstepping the bounds of the assay to use it in every case. In fact it was in the use of a little alcohol for breaking emulsions that the great advantage of its presence was originally determined. If this trace of alcohol is not employed, a fluid extract which is fully up to standard strength might very easily be condemned as having deteriorated to a great extent.

After the alkaloid has been isolated and its exact quantity is to be determined by titration, as with coca, ipecac, belladonna, henbane and stramonium, another error may creep in, especially with the mydriatic leaves and their preparations. The residue left by evaporation of the ethereal or chloroformic solution is to be dissolved in an exact quantity of standard acid and the excess titrated by alkali, but sometimes if much care is not taken, all the alkaloids will not be dissolved even with the excess of acid present and the result of the assay will be too low. To be sure of completely dissolving the alkaloid as is intended in the assay process the addition of 2 or 3 cc. of neutral ether or alcohol is always desirable; not because the alkaloid itself is so difficultly soluble in the acid, but because a certain minute quantity of other substances not easily soluble in very dilute acid is carried through the various stages of the assay and, being incorporated in the final residue, offers more or less protection to the alkaloid against the action of the acid and water. Having effected complete solution by this means it is best to evaporate the ether by brief warming on a water bath, subsequently cooling before titration with the standard alkali; if alcohol is used it may remain in the solution.

Other details in the U. S. P. methods of assay might be cited as possible sources of variation in the results of different chemists as, for example, the apparently very simple process of filtering aqueous or ethereal solutions, but such instances will occur to you from your personal experience in this work and could be multiplied to a great extent.

SUMMARY

Conditions surrounding the assay by different men cannot always be the same and variation may occur for the following reasons:

First and chiefly, because of incompleteness of extraction either of the drug or of the aqueous liquids by immiscible solvents.

Second, by too great haste in carrying out this work, for in chemical assays, as in everything else, the old aphorism that "haste makes waste" is most certainly true.

Third—With particular reference to the fluid preparations of the mydriatic drugs, there is evidence of a peculiar condition in old preparations and sometimes in new ones that prevents the complete extraction of the alkaloid without the use of a trace of alcohol in connection with the chloroform.

Fourth—The question of shaking by hand or by mechanical means at any point in the process may make some difference, but particularly will there be difference in results if sufficient time is not allowed, and it is well to exceed the pharmacopoeial time limit, which is most evidently intended for a minimum statement of time necessary, so that in either case complete extraction will be assured.

Fifth—The solution of the alkaloidal residue in standard acid before final titration may not always be complete, and a little carefully neutralized ether or alcohol should be used as an aid to this end.

Sixth—The individual method of reading end points by various indicators in the titration of alkaloids, while not specifically mentioned above, will have some effect upon the results.

The U. S. Pharmacopoeia has come to be a legal authority and as such will be construed more strictly than ever before, but we must keep in mind that good law is also good common sense, and to apply the pharmacopoeial requirements in any other manner is warping it away from its true purpose.

The carrying out of its assay methods must be done with a clear vision of the end to be attained and a thorough understanding of the many pitfalls in the way of the chemist.

LABORATORIES OF PARKE, DAVIS & CO
DETROIT

WATER SUPPLY FOR THE MANUFACTURER¹

By W. M. BOOTH

Before locating a new plant or industry, a large amount of preliminary information is necessary. Having decided that market conditions, transportation, labor and power are available and acceptable, a thorough study of water conditions must be made. This should determine the quantity, quality, and cost of this material necessary in the production of power, for strictly manufacturing operations, for drinking, for cleaning and for fire. Sum up all possible requirements and add from 50 to 100 per cent for emergencies and for growth.

If possible, two independent sources of supply should be obtainable.

Information of the character demanded can be obtained from a commercial laboratory that has specialized in this direction, or from a consulting engineer who has a laboratory at his disposal. Such a study should be begun at least a year in advance of building operations. Seasonal changes are such that both quality and quantity of water may vary greatly from month to month, if the proposed source is a river, small stream or spring.

Having employed a man or company to make the necessary observations and analyses, the proposed sites can be visited and the requirements pointed out and discussed. If water is to furnish the power of the mill and maximum and minimum flow data are not available, they must be obtained from the government or from original experiments conducted with a weir. Special forms of this device are now sold with recording gauges that read in cubic feet per second. If records have not been kept and the expense of the instrument is more than is thought necessary, actual velocity and depth studies can be undertaken at stated dates each month. If the minimum of these readings shows the passage of the required volume of water, the questions of quantity are dismissed for power, fire and cleaning.

Such water is rarely exactly fitted for power and technical purposes. There is, however, a considerable area of granite or related rock in the United States, the run-off from which is soft and clean. The Adirondacks, the White Mountains, and the Catskills all afford an abundance of soft water. The plants along the streams running from these highlands have many advantages due to this kind of water supply. I have found the hardness to average about fifty parts per million.

Shale rock areas in New York state at an altitude approximating 1400 feet also afford very good water, with a hardness between 100 and 120 parts per million. Limestone areas generally produce hard water. Such a belt runs through the United States from eastern New York to the Mississippi river and south; hardness 150-2000 parts per million. Before use in a power house, this class of water should be softened by chemical means. The cost of treatment varies from a fraction of one cent to twenty cents per thousand gallons.

The quality requirements for manufacturing purposes vary with the nature of the business. Textile mills demand a great volume of soft water, free from iron and sediment. Canned goods concerns need a water under a hardness of 170 parts per million, clean and sanitary, low in organic nitrogen. Power producers and steel plants need large volumes of soft water, free from sediment and oil, and cold for condensing purposes.

¹ Paper presented at the Milwaukee Meeting of the American Chemical Society, March, 1913.

Many industries use water for rinsing. Laundries must avoid water containing iron; in addition it should be soft and clean. Nor can iron tanks be used in storing water for laundries; but wood and concrete are always available.

In fact, very few operations of manufacturers require hard water and in such cases, the necessities are generally well understood.

If a stream cannot be appropriated for a site, a lake may be considered. The Great Lakes serve hundreds of plants. The water has a hardness of from 90 to 100 parts per million. As cheap sources with enormous volume, they are unexcelled. All lake water carries sediment which can be treated according to the needs of the business. One grain of alum per gallon cleans the usual run of lake water at a cost of less than \$2.00 per million gallons.

Smaller lakes in the eastern states are usually on high ground and necessitate a water works system between the source of supply and the plant on the railroad. New York state includes within its borders hundreds of such natural reservoirs. The water has a hardness of approximately 100 parts per million.

Next to lakes, small streams and isolated springs may be considered. The annual maximum and minimum supply must be definitely determined before any plans are made to use such water. Large streams with a large average flow fifty years ago are often dry in midsummer now.

Perhaps the industry does not need a large volume of water daily, or must be situated in a town or city. When there is no choice of location, bad water must be corrected mechanically or chemically. If there is a choice between two or more towns, the question from the water investigators' standpoint is what kind of a supply and what equipment exists at each place.

A complete history of the water works company, plant and equipment should be worked up, short, but showing location and extent of water-shed, storage capacity, piping, pumping plant and the financial standing of the company itself. The quality from a sanitary, mineral and bacteriological standpoint should be made a part of the record, the result of personal investigation and not from published records.

No modern mill superintendent can tolerate a scant supply or a poor distribution system. We all know of towns where the water pressure varies from 20 pounds to zero. Insurance rates are unduly high and fire losses are numerous. Few small towns afford supply in quantity sufficient for big business. My clients operating canning factories require from 50,000 to 100,000 gallons of good water per day for special uses; woolen and cotton mills from 2,000,000 to 5,000,000. Canals and rivers flowing through such towns are the only inducements for large users. City water costs from 3 to 15 cents per 1000 gallons; 10 cents is not unusual. The bill for this item alone may amount to \$30 to \$50 per day. Such a fixed factory cost is not unheard of but it cuts down profits with regular and insistent demands.

If a town will furnish clean, soft water at 10 cents per thousand gallons to a concern using not more than 50,000 gallons a day, the chances are that the use of such is desirable rather than an attempt to find other sources with certain overhead expense and uncertain results.

This statement applies also to wells, fully discussed in my previous paper before the Institute.

DRINKING WATER

No two sanitarians will agree concerning the standard to be set for potable water. In this paper I suggest three types with possible limits of purity. Many thousands of people are drinking each of the three grades daily, with apparently no ill effects.

These tentative standards are as follows:

Parts per million

	I	II	III
Free ammonia.....	0.02	0.05	0.10
Alb. ammonia.....	0.08	0.10	0.15
Nitrates.....	1.00	2.00	2.50
Nitrites.....	0.000	0.005	0.01
Chlorine.....	2.00	10.0	20.0
Oxygen consumed.....	1.00	2.00	3-5
Total solids.....	100.0	500.0	500-4000
Colonies per cc.....	100.0	500.0	1000-20,000
<i>B. Coli</i>	0.00	Presence	
		10 cc.	1/10 cc.
		amts.	amts.
Sediment.....	none	slight	heavy
Color.....	none	slight	yes
Odor.....	none	yes	yes
Temperature.....	winter above 45° F. summer below 60° F.	40° F. 80° F.	very cold very warm

With increased attention to sanitary details everywhere, the manufacturer can well afford to add a clean, pure supply to his factory equipment. If it is impossible to obtain potable water, it should be prepared. In case the supply is muddy, it should be filtered; if polluted it should be passed through sand and charcoal

or distilled and then passed through charcoal. It must be remembered that water distilled from an impure source, organically, carries ammonia and sometimes other gases. Charcoal gives such water a pleasant taste and removes odor. Do not attempt to condense steam from an ordinary boiler for drinking purposes. Rather pass steam through a copper coil in a tin-lined kettle. Condense also in tin. Such water must be cooled before drinking.

When a manufacturing corporation can afford to do so, it should build and operate its own water works. Ten, fifteen, or twenty miles is not a prohibitive distance to go for a good supply. The initial expense will be small compared with the additional resources of the plant that has all of the clean, soft water needed.

To accomplish such a purpose, it may be necessary to buy several hundred acres of cheap land. This should be fenced and all people and animals kept out. Having an abundant supply, a corporation may add to its income by selling water.

If water of a poor quality, but soft, is available near the concern, a purification plant on a large scale can be built to good advantage. Here water may be filtered or softened to the degree required by the average use to which it is put.

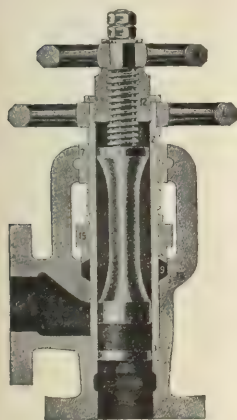
DILLAYE BUILDING
SYRACUSE, N. Y.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE EYNON-EVANS FLANGED BLOW-OFF VALVE

A Philadelphia concern has placed on the market an angle flanged blow-off valve, an illustration of which is shown below. The principle involved is that of protecting the packing inside the shield before the grit, scale and other blow-off products are permitted to pass through the valve from the boiler. The lower end of the shield also acts as a valve, thereby permitting of the removal and inspection of the packing while the blow-off valve is in service with full boiler pressure.



The body and yoke 13 are cast in one piece, and are made extremely heavy. A nickel ring, 3, is secured in the iron body, the interior diameter of which is the same as that of the interior of the bronze shield 2, forming a continuous surface for the reception of the packing. This packing is so placed in the ring 3 and shield 2 that it prevents leakage from the inlet to the outlet and around the stem; it can be adjusted or compressed by the nuts to the desired density while the valve is in service. The hand wheel 14 withdraws the pistons with packing from the ring 3 into the shield 2. The shield 2 is operated by the wheel numbered 11.

Rotating the small wheel 14 causes the packing with its piston to rise or open until the shoulder on the follower piston strikes the bottom of the hub 12. The packing is now inside the shield 2, protected from the blow-off products. Rotation of the wheel 11 causes the shield 2 to rise until the shoulder, just below the thread, strikes the bottom of the threaded bushing 7. After having rotated the wheel 11 to open the valve, and it is now desired to close it, the shield is rotated until it strikes the ring 3. The small wheel 14 is then rotated and the packing is returned to fit inside ring 3, making, it is claimed, the valve absolutely tight. To open, the small wheel is raised first; to close, the large wheel is lowered first.

THE INFLUENCE OF SULFUR ON THE STABILITY OF IRON CARBIDE IN THE PRESENCE OF SILICON.

The value of the heat treatment of the iron-carbon alloys depends mainly upon the manner in which the cementite and pearlite carbide are affected. Especially is this so in connection with the alloys richer in carbon, such as the various cast irons, and Hatfield (*Eng.*, 95, 683) therefore endeavored to make a thorough study of this phase of the subject, as a result of which he recorded some experiments made to ascertain the manner in which sulfur affects the stability of iron carbide.

The influence of sulfur has received considerable attention from the time of Percy onwards, and it is now accepted that, providing the other constituents of normal cast irons remain constant, any considerable increase in sulfur results in an increase in the combined carbon content—in other words, the presence of carbon prevents the entire breaking down of the carbides during the cooling of the iron. It is generally understood that in ordinary cast irons the amount of sulfur present (rarely exceeding 0.06%) has little influence upon the carbon. Wüst has published the results of some experiments which, however, showed that the influence of sulfur was increased by any decrease in the silicon content of the iron. These experiments are considerably amplified by the data contained in a quite recent paper by Coe (*Brit. Foundrymen's Assn.*, 1912).

Hatfield concludes from his experimental investigations that:

- (1) Sulfur increases the stability of iron carbide at high temperatures.
- (2) It is most probably the small percentage associated with the carbide crystals that accomplishes this action.
- (3) Coe's deduction that the sulfur separates as sulfide at the freezing point is not strictly correct, as a small and essential proportion is apparently retained in the cementite carbide.
- (4) The action of sulfur is of a chemical nature, and Levy's suggestion that the action is mechanical and is attributable to the existence of sulfide films does not receive support.
- (5) Silicon in a large measure neutralizes this action of the sulfur, probably by forming a silicon sulfide.
- (6) Manganese neutralizes the action of the sulfur present in such materials as mentioned.

THE ALUMINUM INDUSTRY.

The report, recently issued by the Aluminum Industrie Gesellschaft, which owns the large works at Neuhausen, Switzerland, shows net profits for the year of \$717,000, against \$448,000 in 1911; dividends were 20% against 14% in 1911. The very low prices which prevailed for some time resulted in many new uses being found for aluminum, which favorably influenced the development of the industry and enabled the whole Swiss production to go into consumption. A new agreement has since been entered into by the various manufacturers of aluminum. The subsidiary industries conducted by the Neuhausen works, namely, the manufacture of calcium carbide and nitric acid, have justified expectations, and extensions are being carried out in several directions. The present capital amounts to \$2,500,000 and there are loans to the amount of \$2,070,000.

As to the aluminum industry in the United States, it may be said that the market during the latter part of 1912 was brisk; later the demand has exceeded the supply. The Aluminum Company of America has been making serious efforts for some time past to increase its production, but has been confronted with difficulties in securing an adequate source of supply of electric power. It has, however, secured certain riparian rights in North Carolina and Tennessee. The development of this water power is contemplated. Until its own power development is completed, the Company will use power supplied by the Tennessee Power Company from their development on the Ocoee River, near Chattanooga; this new aluminum plant will, it is planned, be in operation by the middle or latter part of 1913. In addition to its extensions in the South, the Aluminum Company is engaged on an extension to its Massena, N. Y., plant, which, when completed in 1914, will make that plant the largest of its kind in the world. A large supply of electricity will be brought to Massena from the development on the St. Lawrence at Cedar Rapids.

The Aluminum Company of America has recently embarked in the manufacture of powdered aluminum, which is employed in explosives, lithographing and printing, and as a paint pigment; the concern has in operation at New Kensington, Pa., one of the most complete aluminum bronze plants in the world. This plant was recently moved from Dover, N. J. Tanks, cooking vats, and similar vessels are also being made at the New Kensington plant; a considerable extension has been made to the cooking utensil factory located at this point, and a thoroughly modern boiler house is also being installed.

The most notable growth in the industry during the past year has been in extruded forms, tubing and aluminum foil. The Aluminum Company is planning a considerable extension to its tubing plant at New Kensington, and is erecting an aluminum foil plant at Arnold, Pa.

ELIANITE.

The electrochemical works of Rossi in Legnano has, for some time, been conducting experiments on the production of acid-proof alloys, and it is now announced that it has succeeded in obtaining one cheaply. The new alloy—"elianite"—is produced in an electric furnace and is to be used in the manufacture of nitric acid from the air; it is said to differ from similar alloys known in that its resisting power is not limited to certain acids, and it is a good conductor of heat. The composition of "elianite" is kept secret.

THE INDUSTRIAL USES OF CALCIUM CARBIDE AND ACETYLENE.

In an address on the industrial uses of calcium carbide and acetylene, and their influence on the development of other industries, delivered before the Verein österreichischer Chemiker (*Z. angew. Chem.*, 26, No. 36, 318), Fraenkel referred to a paper

read by him before the same society five years ago. At that time, most of the calcium carbide was consumed in the production of acetylene for illuminating purposes, while very little acetylene was used for autogenous welding; now, however, as much calcium carbide is employed for the production of acetylene for welding purposes as for use as an illuminant. The latter application has nevertheless opened up new fields for the use of calcium carbide and acetylene, particularly in mining and on railroads and steamers.

The development of the autogenous welding industry has led to a great increase in the consumption of oxygen. According to Linde, the German production of oxygen from liquid air amounted to 30,000 cubic meters in 1903, while about 2,000,000 cubic meters were produced in 1910; Vogel estimates that 5,000,000 cubic meters were manufactured in 1912. The successful application of acetylene and hydrogen in autogenous welding led to the employment of a number of other compressed gases and liquids (illuminating gas, oil gas, Blau gas, ethane, benzol, benzine, alcohol, etc.) for the same purpose. Fraenkel considers, however, that the results obtainable are inferior.

The production of cyanamide from calcium carbide induced the establishment of a nitrogen industry. Nitrogen is obtained from liquid air by the process of Linde and Claude. Fraenkel discussed the production of cyanamide, and predicted still further development to the production of ammonia with the simultaneous manufacture of formic acid (a suggestion from Sulzer). He further anticipated development of the processes of Hubou, Machtoff and Morani, for the decomposition of acetylene into carbon and hydrogen, and of the method of Frank and Caro for the preparation of carbon. Machtoff's process is being operated by the Caronium Gesellschaft in Friedrichshafen, the pure hydrogen obtained being used by the Zeppelin Gesellschaft and the carbon in the manufacture of inks and varnishes, especially in Russia.

Fraenkel touched upon the production of chlorine derivatives of acetylene and appeared to be enthusiastic concerning the future of trichlorethylene as an industrial solvent. He pointed out that the technical solution of the problem of producing acetaldehyde from acetylene by the action of water appeared to have been successfully accomplished by the Griesheim-Elektron A.-G. and Grunstein. The reaction is accomplished best in sulfuric or phosphoric acid solutions, mercury salts serving as catalysts. The aldehyde-paraldehyde must be quickly removed from the solution in order to avoid polymerization. The aldehyde may be oxidized to acetic acid or reduced to alcohol.

In order to obtain cyclic compounds from acetylene, Fraenkel recommended the Richard Mayer modification of Berthelot's pyrogenic condensation; he also commended the process of Steinkopf for the preparation of thiophene. Finally, he predicted that acetylene would be employed in the synthesis of caoutchouc: a mixture of acetylene and ethylene may be condensed at a red heat into butadiene, which can be transformed, by methylating, into isoprene.

THE EMPLOYMENT OF LIQUEFIED GASES IN MINING AND METALLURGY

It is reported in *Echo des Mines*, 1913, 476, that liquid air and liquid oxygen are being experimented with in Germany as mine explosives. Liquefied oxygen, mixed with aluminum powder, and detonated, forms, it is said, an explosive about 2½ times as powerful as black powder, from which there is no production of deleterious fumes.

The same journal comments favorably upon the use of liquid air to attain high temperatures in metallurgical operations. It is stated that a Thomas furnace is being worked at Ougree-Maripaye by injecting liquid oxygen, under pressure, into the hearth, where it raises the temperature to 2000° C. The claim is made that large quantities can be treated, as with coal or coke,

much more easily than in an electric furnace; that the reactions occur quickly without any change in the *modus operandi* usual in steel-making; and that the fusion time is reduced one-half and a furnace can double its output. Some trouble has, however, been experienced in maintaining the furnace walls, owing to the high temperatures.

THE STORAGE OF INFLAMMABLE LIQUIDS

At the Seventeenth Annual Meeting of the National Fire Protection Association, held in New York, May 13-15, 1913, about one-half of the report of the Committee on Laws and Ordinances was devoted to a suggested complete ordinance to regulate the use, handling, storage and sale of inflammable liquids, etc. It was explained that this was the completed work of several former committees and that the ordinance was much desired throughout the United States. Inflammable liquids were classified in accordance with their flash-point. Class 1, the most dangerous, included ethyl ether, carbon disulfide, gasoline, naphtha, benzole, collodion, "hydro-carbon" ("gas-drips"), and liquefied petroleum gas. Class 2 embraced acetone, alcohol, amyl acetate, and toluol. Class 3, the least dangerous, included kerosene, amyl alcohol, turpentine, whisky, and brandy. Severe restrictions were placed on the storage of Classes 1 and 2, although in a few minor ways Class 2 was to be treated similarly to Class 3.

Strong objection to the classification on the basis of flash-point alone was raised by those interested in the manufacture and sale of alcohol for commercial use. It was claimed that the actual fire hazard was not in proportion to the flash-point, which placed alcohol in Class 1, but that it was greatly reduced through the lightness of alcohol vapor and its rapid diffusion in air to a non-inflammable and non-explosive mixture, together with its miscibility, which prevented the burning and vaporizing liquid from being scattered by water. These disputed points are to receive investigation by the committee.

[It may be stated on the authority of von Schwartz ("Fire and Explosion Risks," 1904, p. 270) that "in point of general fire-risk, alcohol is far below ether, benzol, carbon disulfide, and similar liquids." Alcohol between 60 and 99.5% strength is more inflammable than ordinary petroleum; but the vapors are far less explosive, since, in order to attain this condition, they require to be strongly heated and placed in contact with a flame or spark. Special danger attaches to alcohol by reason of its high diffusibility; the stronger the alcohol, the more rapid is the dispersion.—W. A. H.]

FUEL BRIQUETTING IN THE UNITED STATES

Fuel briquetting in the United States in 1912 is discussed by E. W. Parker in an Advance Chapter from *Mineral Resources of the United States for 1912* (U. S. Geological Survey, 1913). Although the quantity of briquetted fuel manufactured in the United States in 1912 did not show any material gain over the preceding year, the industry may be considered as passing out of the experimental stage and assuming more of a substantial and permanent character. The total quantity of briquetted fuel made in this country in 1912 was 220,064 short tons, valued at \$952,261, as compared with 218,443 tons, valued at \$808,721, in 1911. There were nineteen plants which contributed to the production in 1912; of these, 9 in the Eastern States produced 107,181 tons, 7 in the Central States produced 89,714 tons, and 3 on the Pacific Coast produced 23,169 tons. Seven plants used anthracite culm, 9 used bituminous or semibituminous slack, 1 used carbon residue from gas manufactured from oil, 1 used mixed anthracite culm and bituminous slack, and 1 used peat. Two plants, 1 at Detroit, Mich., and 1 at Point Breeze, Philadelphia, Pa., which were constructed for the purpose of principally utilizing coke breeze, were not operated in 1912,

the abrasive action of the coke dust being so destructive to the molds and machinery that the plants have been closed.

Among the indications of the interest taken in the briquetting industry as promising future development are the following:

1. The organization of the Malcolmson Briquet Engineering Co., of St. Louis, Mo., for the purpose of designing, building, and equipping briquetting plants, but not for the purpose of engaging in the manufacture of briquets.

2. In contemplation, the construction of a plant for the manufacture of boulets by the Devillers or Belgian process at Grafton, W. Va., which shall utilize bituminous slack from the mines of the Grafton district.

3. In contemplation, the construction of a plant at Cambridge, Mass., by the Atlas Coal Briquet Co., with headquarters in Boston. It is reported that the contract has been closed for the construction and equipment of a plant similar in design and character of output to the one in Brooklyn, N. Y.

4. Under construction, the plant of the Northern Briquetting Co., at Minot, N. Dak., for the purpose of utilizing lignite, of which ample supplies are available. The plant is expected to be in operation in August, 1913.

5. In contemplation, the Pacific Coast Coal Co., Seattle, Wash., expects to have a plant completed by October, 1913. The character of the fuel and the binder to be used are not stated.

"PAROL"

A new fuel for use in internal combustion engines has recently attracted attention in Johannesburg, South Africa. This gasoline substitute, now being marketed under the name of "Parol," is said (*Chem. World*, 2, 175) to be made from paraffin by a chemical process and without the use of heat. It is claimed by the manufacturers that, by means of the chemical process employed, the property which creates carbon in the cylinders and forms soot around the sparking plug is eliminated; the paraffin used in all the tests so far is of 150° fire test. The manufacturers contemplate going to England in the near future to compete in the tests to be conducted by the Royal Automobile Club for fuels other than petrol.

SOLID ALCOHOL

The methods used in the preparation of solid alcohol may be classed in three categories (*Chem. News*, 107, 257).

The first consists in fabricating a solid soap into which alcohol is mechanically incorporated; in this manner a translucent product is obtained containing 60 per cent of alcohol. Instead of employing soap as a vehicle, the alcohol may be enriched with collodion; the process is more expensive than the preceding one, but it gives a more satisfactory product, because of much easier combustion and of a more engaging exterior aspect. Usually alcohol soaps are delivered by trade in the form of a paste enclosed in a metal box made in one piece, which can be used as a warmer, the cover of which has openings that can be regulated, so as, if need be, to act as moderator to the flame; on the contrary, the collodions of alcohol are arranged for sale in the form of pills or ovals, almost transparent. Both soaps and collodions are too expensive to be practically utilizable as industrial combustibles; their employment is restricted to applications of luxury, such, for example, as being burned in toilet-lamps, traveling spirit lamps, etc. However, it is not the same for the little bricks of sawdust impregnated with alcohol and agglutinated with coal-tar that are just now being brought out in trade at a low price, and which may turn out to be a practical combustible.

BENZOLE AS A MOTOR FUEL

We learn from *The Chemical Trade Journal*, 52, 569, that the committee appointed by the Automobile Club and kindred

associations is working in a very energetic manner to popularize the use of benzole as a motor fuel and also to stimulate its production. Toward the end of May, Lord Montague of Beaulieu brought together a number of people interested in gas undertakings, for the purpose of hearing the proposal of H. L. Doherty, of New York, relative to the extraction of benzole from coal gas. Briefly stated, the proposals were to extract the benzole from the coal gas for use as a liquid fuel and to supply gas having no illuminating power. To quote from the same source: "Now that the calorific standard for town's gas is being more extensively adopted, and also having regard to the fact that the illuminating power is not of itself an important point, the presence of benzole in the gas is not essential, but whether it would pay to extract it from coal gas is quite another matter no one seems to know how much benzole is contained in coal gas as produced under existing conditions. If the quantity is anything less than two and a half gallons per ton of coal, . . . it will be seen that very little margin for profit will accrue to the gas works."

Brewer (*Idem*, 52, 572) showed, at the meeting of the Institute of Inventors, that his experiments with benzole proved it to be a suitable carburant.

A NEW PRODUCT FROM WHALE OIL

A German-Norwegian company, capitalized at about \$833,500, organized to work a new German method for hydrogenating whale oil, commenced operations at Fredrikstad, Norway, in May. The Hafslund Falls are being utilized to generate the electric power required by the works and also to manufacture by electrolysis the hydrogen required for the hardening process to which the purified whale oil is submitted and converted into a solid neutral fat. The daily consumption of oil is about 300 barrels.

[Bömer and Leschly-Hansen (*Chem. Rev. Fett. Ind.*, 19, 218, 247) hardened whale oil by the method of Wilbuschewitsch, according to which the oil is mixed with the catalytic agent (nickel reduced on kieselguhr) and heated in an autoclave under pressure while a current of hydrogen is introduced. The product possessed a melting point of 45.1° C.; a solidifying point of 33.9° C.; an acid value of 1.2; a saponification value of 192.3; an iodine number of 45.2; and a refractometer reading at 40° C. of 49.1.—W. A. H.]

THE COMPOSITION OF SOME SOLE LEATHERS

Investigations conducted by Veitch and Rogers (*Bull.* 165, Bureau of Chemistry, U. S. Department of Agriculture, 1913) show that weighting of leathers with useless or harmful materials is largely practised in this country, with the result that resources in leather materials are wasted and the public is defrauded. A large majority of the samples examined contained an unnecessary quantity of uncombined tanning material; in fact, Veitch and Rogers estimate that but little less than \$1,000,000 worth of tannin is wasted annually in this way. Sixty-three per cent of the leathers examined were weighted with glucose, with Epsom salts, or with both. The amount of loading varied from 1 to 7.3 per cent of Epsom salts, with an average of 3 per cent; the maximum quantity of glucose in the loaded leathers was 10.4 per cent, and the average 5.5 per cent. The maximum amount of these loading materials found in any leather was 16 per cent and the average where both were present was 8 per cent. The results obtained indicate that not less than 12,000,000 pounds of glucose and Epsom salts are sold annually in sole leather to the American people. With regard to the weighting of leather, Veitch and Rogers conclude that the materials add absolutely nothing to the wearing value of the leather and where present in large quantity may positively decrease its wear. Shoes made from these leathers are readily penetrated by water. Loading makes leather more

costly, consequently an inferior leather is more expensive than a good leather.

A NEW HORN SUBSTITUTE

A process which combines leather and celluloid has been devised in Germany for the production of a horn substitute. The hide is depilated and then extracted with amyl acetate and acetone, to remove fleshy matter and to produce a hardening effect. Subsequently it is coated with a solution of celluloid in amyl acetate and acetone. When the solvent has evaporated, the hide is placed in a bath of shellac dissolved in alcohol. It is said that hide thus treated is not only similar to horn, but also possesses its elasticity and strength; the product is strong and light, and is suitable for the manufacture of trunks, boats, and insulating materials.

SOME INDUSTRIAL USES OF SUGAR

A list of the industrial applications of sugar, which illustrates the great diversity of manufactures in which this product appears quite apart from food economy, was contributed by Rolfe to *The Chemical News*, 107, 217.

French writers, especially Vivien, have recently made pleas for the use of sugar as the cheapest form of pure carbohydrate, since it replaces, in many cases, glucose, starch and dextrin. The French Government imposes a tax on sugar and glucose products used as human foods, but "denatured" sugar is exempt from taxation. As in alcohol denaturation, the substance added is, if possible, some ingredient in the special process using the sugar. In France, an excellent quality of sugar known as No. 3 white sugar and polarizing over 99 per cent sells, when denatured, at a lower price than does starch, glucose or dextrin, approximating what the refiners pay here for raw sugar.

Sugar is a common ingredient of many compounds for removing and preventing boiler-scale, and as these usually contain alkali, this is used as a denaturant. The shoe-blackening industry uses sugar and molasses to a considerable extent. In Europe there seems to be a tendency to use blackings of this older type as less injurious to leather than the newer wax blackings, owing to the solvents used in the latter. These shoe-blackings are made by the carbonization of sugar with sulfuric acid, neutralizing the product, and then incorporating boneblack, oil, etc. Many tons of sugar are now used by manufacturers of transparent soaps; sugar soaps are less sticky than glycerin soaps. There are over thirty patents for explosives in which sugar is a component to the extent of from 6 to 40 per cent. This use of sugar has become so important in Germany that a special provision is made in that country for denaturing sugar employed in the manufacture of explosives, paraffin being used. In the color and dyeing industries sugar is used as a reducing agent in indigo and chrome work, as a base for the manufacture of organic chromium salts, and as a vehicle or "filler" for solid aniline colors, giving them an attractive appearance. The European tanneries use large amounts of sugar in "filling" leather and, to some extent, in removing lime from the hides in dehairing. This solvent action of sugar on lime, and the easy recovery of the sugar by carbonization, has suggested its use in several processes where it is desirable to remove excess of caustic lime from calcined minerals, such as phosphates, magnesium oxide, etc. Tannin extracts are also "filled" with sugar, as they are in the United States with glucose. Sugar is also used in several chrome tanning processes as a reducer, and, as in dyeing, for making acetates and formates. Still other uses are in the manufacture of copying inks, printers' rolls, hektograph pads; silvering of mirrors, hardening of mortar and plaster; as a source of pure carbon for use in the manufacture of pure carbon monoxide or sulfurous acid; and as a source of sucrose octonitrate, or nitrosaccharose, a product analogous

to guncotton, sucrose acetate, a substitute for cellulose acetate, and sucrose benzoate.

PAINTS FOR INDICATING THE USES OF PIPES

Engineering, 95, 607, states that in 1911 German engineers and metallurgists came to a preliminary understanding that it was desirable to mark pipes carrying certain fluids by certain colors, so as to avoid confusion. The question has since been discussed by technical institutions and chemical manufacturers. It was natural that conflicting wishes should be expressed, for in each works some particular kinds of pipes may predominate or coexist, and the managers naturally desire to make certain distinctions particularly easy. The majority of authorities have, however, now agreed that the following colors should be used for the following purposes: Water, green; gas, yellow; air, blue; steam, white; acid, pink; lyes, violet; oils, brown; tar, black; and vacuum, gray. It is recommended that pipe conduits for high tension electric currents be marked red, like acids, as red would be the danger color; the forked-lightning arrow might be added as a distinctive mark. It is proposed that an ordinary steam-pipe should be white; a red ring would indicate a pressure of more than 2 atmospheres; 2 red rings, high-pressure superheated steam; and a green ring would distinguish the exhaust-pipe. A dark red ring on a pink or violet acid or lye pipe would intimate that the acid or lye carried was concentrated. A black ring would stand for carbon or an impurity; a tar-oil would be brown with a black ring; a refuse-water pipe green with a black ring. Pipes for ordinary gas or for purified blast-furnace gas would be painted yellow; the red ring might indicate coke-oven gas, the black ring blast-furnace gas not purified, the green ring water-gas, the blue ring producer-gas, etc. In blue air-pipes the red ring would indicate high pressure, a white ring hot air. Potable water pipes might be green with white dots; pipes carrying slimes, green with black dots. Letters might be employed to distinguish different gases and liquids. Small iron labels or rings a few inches in width, properly colored and then varnished or enameled, would cause much less expense. It is the opinion of German engineers that enameled rings, directly clamped around the pipes, are most convenient.

A SELF-EQUALIZING EXPANSION JOINT

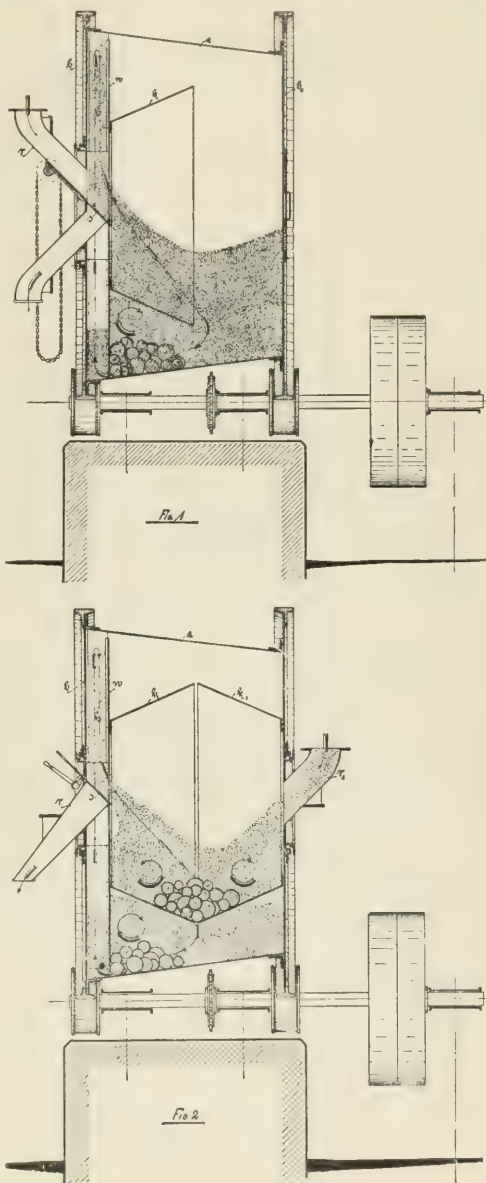
The "Badger" self-equalizing expansion joint is a corrugated copper joint having external rings and is designed to take up changes in length of pipe lines conveying steam, water or air. The external rings on the corrugations distribute the strain and by thus bringing many corrugations into service no one of them is called upon to take more than its share of the strain. The rings force a part of the strain to the next corrugation, and, as each corrugation has only a slight movement, the joint is said to last almost indefinitely. The number of corrugations depends upon the pressure and upon the length of the joint. For high pressures and superheated steam the change in length is considerable, and, therefore, more corrugations are used; for very low pressures, as in exhaust piping, 2 or 3 are sufficient for the slight alteration in length. In some cases where the expansion is small but the vibration must be taken up, the joint does not require any external rings; these, however, add strength and also stiffen the exhaust pipe against collapse. This new joint is said to require no packing and to take up no more room than a pipe fitting.

A NEW TYPE OF PULVERIZER

A German firm has placed on the market a pulverizing machine with conical cylinders, and constructed in such a manner that it is dust-proof and perfectly automatic. It is designed to grind substances to a fine state of subdivision and to simultaneously

produce intimate mixtures. The construction is shown in the accompanying figures.

This pulverizer is claimed to be more efficient than any other type for the following substances: chemical products, mineral colors, dyes, feldspar, barite, ores, chalk, gypsum, clay, white lead, lithopone, ultramarine, resins, saltpeter, salt, lime, coal,



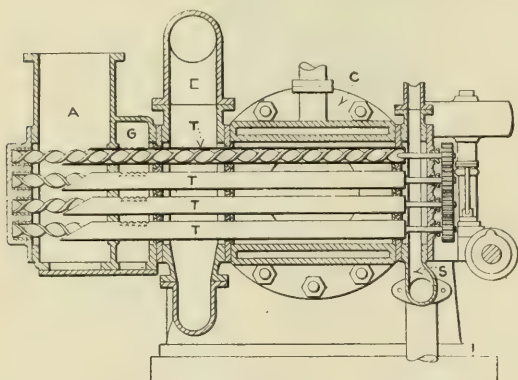
cement, sand, coke, cork, flour, manure, graphite, chamotte, etc. It is claimed that the machine is particularly useful for mixing aniline dyes with vegetable dyes.

The material is charged into the conical drum by way of a fixed hopper. At the base of the drum is a scoop which returns the material to the drum at every revolution, thus effecting intimate grinding and mixing. A man-hole is provided on the side for cleaning the interior of the drum.

THE LOW GAS PRODUCER AND ENGINE

A. M. Low has invented a self-contained unit for the direct conversion of coal energy into work. It is essentially a producer-gas engine with a compact gas producer attached to the end of the cylinder. The illustration shows a 100 h. p. unit, which is said to have developed a brake horsepower hour on $\frac{1}{2}$ lb. of coal.

Coal is fed into the hopper A, from which it is conveyed by four worms through the heater tubes T. These tubes pass through the gas chamber G, connected with the inlet valve, the exhaust-heated chamber E, the combustion chamber C, and open into the ash and soot chamber S. The latter is fitted with a non-return valve, which admits air or a mixture of steam and air to the tubes. This air is drawn by the suction of the engine over the incandescent coal, maintained in this state by the heat of chambers C and E, and passes through holes in the tubes T into chamber G. It is by this time mixed with the gases given off from the incandescent coal, and the mixture passes



from chamber G through the inlet valve into the cylinder of the engine.

In starting, the coal is brought up to incandescence by running for a few minutes on illuminating or other available gas. The feed of the worms, which are driven through gearing at the right, may be adjusted to suit the load, and the coal, after it has given off all its gas, is discharged as ash into the bottom of the ash chute S.

Trouble from the formation of tar, which might have been expected, has not been experienced, as the tar is not gasified, but passes entirely off as a fine yellow dust. The rapid heating of the coal in small quantities causes this, and the high temperature and relatively low compression, about 90 lb., prevent condensation and precipitation in the engine passages.

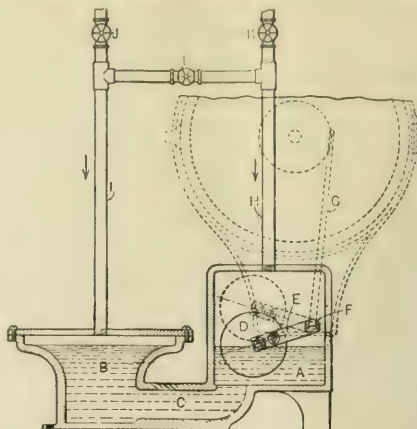
A NEW TYPE OF RECORDING DIFFERENTIAL PRESSURE GAUGE AND RECORDING FLOW-RATE METER.

The new float type Bristol recording differential pressure gauges are designed to record differential pressure or differences between two pressures, or to record changes of level of liquids in closed spaces under pressure.

One of the special features of these new float type recorders is that they can be constructed to accurately record on charts having scales graduated uniformly in terms of velocity or volumes of air, gases, steam or liquids flowing. Another special feature is their ability to withstand sudden fluctuations of differential or static pressure and at the same time produce accurate records of rate of flow of volumes or quantities of liquids or gases flowing. These float type recorders are made for both high and low ranges of differential pressure, and may be subjected to either heavy or light static pressures.

Among the numerous applications for recording differential pressure gauges, some of the most important are for recording rate of flow of air, gases, steam, water and other liquids, in connection with Pitot tubes, Venturi meters, orifices, nozzles, and combinations of Pitot tubes and orifices or nozzles.

The extreme simplicity of construction and the absence of



multiplying devices and all other complicated mechanisms make these recorders especially suitable for practical service under ordinary operating conditions in manufacturing plants and industrial works, such as steel works, blast furnace plants, power plants, gas works, by-product coke plants, water works, natural gas systems, chemical works, etc. The accompanying figure shows a cross-sectional diagrammatic sketch outlining the fundamental principles of construction and operation of one model of float type recording differential pressure gauges. It will be noted that there are two pressure chambers, A and B, intercommunicating through the connection C. In this way the pressure casing forms a U tube, and the liquid employed for low ranges of differential pressure is sometimes water and the liquid employed for high ranges of differential pressure is usually mercury. In the pressure casing A, a cylindrical float, D, is outlined, and this is connected rigidly by arms to the shaft F, to which the pen arm G is rigidly fastened. The rise and fall of the liquid in the pressure chamber A, therefore, causes the float and pen arm to move about F as an axis. The dynamic or high static pressure is applied to the surface of the liquid in the compartment B through the pipe I and the low static pressure is applied to the surface of the liquid in the compartment A through the pipe H. When the static and dynamic pressures are to be applied, the by-pass L is first opened, and then the valves J and K are opened, and later the by-pass L is closed, so that the difference between the two pressures acting on the liquid in the compartments A and B will produce corresponding differences of its level in these compartments, thus causing the pen to record the differential pressure.

By making the cross section of the pressure chamber B of certain proportions, as indicated, it is possible to produce a scale whose graduations are uniform for equal increments of flow of volume. The Bristol-Durand Radii Averaging Instrument may be used on chart records obtained from this instrument for integrating the total flow during a period of 24 hours.

THE STATUS OF THE CERESIN INDUSTRY

The present condition of the ceresin industry is discussed by Lach in *Chemiker-Zeitung*, 37, No. 56, 573.

Owing to the high price of Galician ozokerite, the ceresin industry is in a serious position; the market price of ceresin has

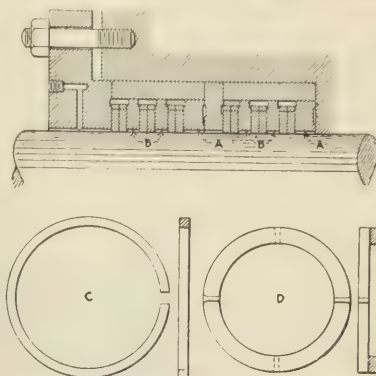
advanced and accordingly the consumption has decreased. Recently two innovations having a technical bearing upon the ceresin industry have appeared. One is a variation in the process of manufacturing potassium ferrocyanide; the other is the introduction of magnesium hydrosilicate as a decolorizing agent. It has been demonstrated at the "Frankonit" works of the Pfirsinger Mineralwerke G. m. b. H., at Kitzingen on Main, and at the "Tonsil" works of the Tonwerke Moosburg, A. & M. Osterrieder, in München, that the ceresin bleached with silicate is superior to that decolorized with bone-black; this may be accomplished at one-half the cost. Partially refined ceresin is treated only once with concentrated sulfuric acid, and a finished product is obtained by treatment with 3 to 5 per cent of "Tonsil," instead of subjecting ozokerite to two treatments with sulfuric acid, thereby occasioning a loss of 20 per cent.

HORTON GAS-ENGINE PACKING

A new packing for large gas-engines has been designed by James Horton, of the Carnegie Steel Co. It is claimed that excessive friction and wear on the piston rod is eliminated by preventing the closing of the collapsible ring under excessive pressure.

As shown herewith, the packing rings proper *C* and *D* are in contact with the rod. They are placed in grooves, the walls *A* and *B* of which are free to move in line with the rod and thus

bind the packing rings against forcible closing at the time of the highest pressure in the cylinder. In practice it is found that this side clamping of rings does not affect the sealing quality



ROD PACKING FOR GAS ENGINE

of the packing, as contact with the rod is sufficient to prevent the passage of gas, but yet so light that wear cannot be detected on the rod. All rings and corresponding parts of the packing are interchangeable.

SCIENTIFIC SOCIETIES

PROF. DR. PAUL WALDEN, PRESIDENT OF THE NINTH INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY

By GEORGE FREDERICK KUNZ

Received Jan. 11, 1913

At the Eighth International Congress of Applied Chemistry, held in New York, last September, the celebrated chemist Prof. Dr. Paul Walden, of Riga, was selected to serve as president of the Ninth Congress to be held in St. Petersburg in 1915. No more fitting choice could well have been made, for the great and important services rendered by Prof. Walden to the progress of chemical science are universally acknowledged in the scientific world.

Born near Riga in the province Livonia, July 27, 1863, the new president is by birth a Russian, although of German blood. His early education was obtained at the Real-school in Riga, and later at the Riga Polytechnicum. Here he had the privilege of studying under the great Ostwald, then professor of chemistry at this institution, and he was soon recognized to be one of the most apt and brilliant pupils of his master. In 1885, he was appointed assistant in the department of physics, and in 1888 in that of chemistry. The year 1892 saw him privatdozent, and two years later he became professor of analytical and physical chemistry. He is now, and has been since 1896, assistant professor of inorganic and physical chemistry and a director of the Riga Polytechnicum. On Ostwald's resignation of the professorship of chemistry there, Walden became his successor, and he still holds this position. His degree of Doctor of Philosophy was given him at Leipzig in 1891; in 1893 the degree of Master of Chemistry was conferred upon him at Odessa. Then followed the degree of Doctor of Chemistry from the University of St. Petersburg, and that of Doctor of Engineering from the Riga Polytechnicum. He has laboratories both in Riga and in St. Petersburg.

Russia has not failed to honor the attainments of one of her greatest citizens, Walden having received many important Russian decorations. He is commander of the Order of Vladimir as well as of those of St. Anne and of Stanislaus. The Russian Academy of Sciences has elected him one of its

members, and he is also an honorary member of the London Chemical Society. He was the Imperial Russian delegate to the Eighth International Congress of Applied Chemistry.

Prof. Walden's thorough command of a number of spoken languages will greatly facilitate the performance of his duties as presiding officer of the International Congress. Russian, French, German and Livonian he speaks fluently, and he is thoroughly familiar with English and Italian as well. His quiet, dignified manner, coupled with a large share of mental and physical alertness, can also count as an important asset. Some five feet eight inches in height and weighing about 175 pounds, with blue-gray eyes and fine teeth, and wearing his hair brushed high up on his forehead, his appearance is very prepossessing. When addressing an assembly, his words come readily and his forceful, direct delivery brings them home to his hearers. His thought seems to clothe itself spontaneously and naturally in well-chosen and effective words and phrases; there is no touch of ambiguity in his clear-cut sentences and they always convey to his auditors the strictly logical sequence of his ideas and deductions, convincing them that his statements are the outcome of ripe reflection and dictated by sound judgment.

It is for his extended investigations in the field of stereochemistry, and for his more recent epoch-making work on non-aqueous solutions, that Prof. Walden is best known. He began his scientific career, under the inspiration of his great teacher, Ostwald, with a series of investigations directed to the determination of the constitution and molecular weights of salts in aqueous solution by means of electrical conductivity measurements.

After Ostwald left Riga for Leipzig, Walden turned from physical chemistry to organic chemistry. First in collaboration with his teacher and colleague, Bischoff, and later independently, he carried on a long and important series of researches in the field of stereochemistry. Conspicuous among the achievements of Walden during this period may be mentioned his collaboration with Bischoff in the preparation of the well-known "Handbuch der Stereochemie," the discovery of the important phenomenon since known as Walden's inversion, and

the recognition of the bearing of the optical activity of natural petroleum on their origin and mode of formation. In 1904 Walden summed up the then state of knowledge of stereochemistry in a notable lecture delivered before the German Chemical Society.

More important, however, than his work in the fields of stereochemistry are his investigations upon non-aqueous solutions. Beginning in 1900 with the discovery of sulfur dioxide as an electrolytic solvent, his work in this field continued uninterruptedly to the present time and has included a detailed study of the physical properties of solutions in practically every available solvent, organic and inorganic.

The electrolytic dissociation theory of Arrhenius had its origin in the exceptional behavior of water solutions as contrasted with solutions in non-aqueous solvents, and while certain non-aqueous solvents at the time Walden began his work were known to form solutions which are conductors of electricity, the data at hand could not be brought into harmony with the general laws which had been developed in connection with the study of aqueous solutions. Indeed, it was pretty generally believed that these laws did not apply to non-aqueous solutions.

It is to Walden, more than to any other contributor to the knowledge of solutions, that credit is due for showing that instead of being limited in its scope, the electrolytic theory of Arrhenius is applicable to all electrolytic solutions without exception, non-aqueous as well as aqueous.

Walden has given his exceptional talents almost exclusively to the development of pure chemistry. He has contributed little or nothing directly to applied chemistry.

Aside from his purely scientific activity Prof. Walden has found time to write several biographical sketches and memoirs of noted scientists of our day, these studies being marked by keen and critical insight, by a thorough comprehension of the special endowments and qualifications of the men, and by a luminous exposition of the great scientific truths which they proclaimed and illustrated. Berthelot and thermochemistry, Pasteur and the germ theory of disease, the Russian Mendeléeff and the periodic system of the elements, have all been brought nearer to the reader's understanding by Walden's biographical memoirs.

The most important and significant of these studies, however, is that devoted to the life and work of his venerated master and friend, the widely-famed physical chemist and philosopher, Wilhelm Ostwald. Here it was indeed a labor of love that Walden performed, and so well has he done his work that Ostwald himself has been heard to say that a full half of his great

reputation could be justly ascribed to the influence exerted by this sympathetic study of his career and activities.

In addition to the very extensive original work of Prof. Walden, he has enriched Russian scientific literature with several translations of noteworthy scientific productions into that language. Such, for instance, as Fischer's "Anleitung zur Darstellung organischer Präparate," and the "Lowell Lectures" delivered by the renowned chemist J. H. van't Hoff.

Possessed of such wide and varied attainments as is Prof. Walden, he seems to be an ideal choice for president of the Ninth Congress. Many qualifications not often united in the same individual are most essential for success in such a position. The delegates, coming as they do from all the principal countries, represent not only the scientific culture of these lands but also

the diverse endowments and characteristics of many nationalities and races. To bring about among them a harmonious interaction in the true interest of science is not always an easy task, but it is one that may perhaps be best accomplished by a scientist having the intimate knowledge of the art of combining chemical elements possessed by Prof. Walden, and we are fully confident that all the delegates of the coming congress will find in him one whose devotion to pure sciences has in it no touch or stain of national partiality or prejudice. The question as to the number of official languages, whether three or four, to be used in the Ninth Congress, came up before the Eighth Congress and the decision favored the recognition of the four languages, English, French, German and Italian.

Of great importance to the scientific world was the recommendation by the Eighth Congress that an agreement should be reached providing that the atomic weights recognized by one of these triennial Congresses of Applied Chemistry should be regarded as standards until changed by a succeeding

congress. This would be a means of securing uniformity in all industrial and scientific uses. A standard governmental examination of ores, metals and fuels was also strongly advocated as of prime importance for mine owners, as well as for all distributors and consumers of mining products.

When the Ninth International Congress assembles in St. Petersburg in 1915, a number of questions touching the organization and management of this assembly will come up for consideration, such as the proper placing of the international delegates and the proper assignment of the papers to be read, in order to determine the due attribution of priority to one nation or another in reference to scientific or industrial discoveries of which so many are constantly being announced in this age of feverish activity in all departments of science and industry.



PROF. DR. PAUL WALDEN

Another subject for consideration will be the founding of a Congress of Congresses with its headquarters at the Hague.

In accepting the presidency of the Ninth International Congress Prof. Walden spoke (in German) as follows:

"The choice which has just fallen upon me is a distinction of an altogether exceptional kind, and also a task of an exceptional kind. On behalf of Prof. Kononoff, who is absent, and who will assuredly regret his inability to take part in our common celebration, I can express to you only his thanks and his undoubted acceptance. In my own case, however, I realize mixed emotions. I say to myself: 'Much honor, much work; many disappointments, many gray hairs!' In accepting this choice, we are fully aware that our powers will prove insufficient to do full justice to the duties entailed, but we see therein an honor rendered to our fatherland and to the great men, the great chemists of our country. I need recall to your minds only a few names; that of Lomonosoff, who 160 years ago laid the foundation of modern chemistry; that of Grotthus, a Russian chemist of a century ago; that of Hessen, also a chemist; and finally I name to you our great fellow-countryman, recently deceased, Mendeléeff, the creator of the periodic system of the elements. I assume that the honor you have just accorded to our fatherland is also addressed to these great men. We are the inheritors of the deeds these men accomplished. It is not the mind alone that rules congresses, the heart also must have its say. Of the scope of my mind, I am, naturally, not qualified to speak, but in what concerns my heart, in what concerns my ardent wish to do my best to give you the best possible reception, as to this I believe I can safely speak, as to this I shall willingly and gladly compete with the gentlemen who have received us in former congresses, and if three years hence, in transmitting my office into other hands, I may perhaps be able to speak in my turn with the sunny humor of our president of to-day, then I shall be content. I thank you."

The following list embraces the principal works and articles published by Prof. Walden, and testifies to his tireless activity in the domain of physical chemistry:

- "Die Affinitätsgrößen einiger organischen Säuren." (Dissertation), 73 pp., 8vo, Leipzig, 1891.
- "Versuch zur Untersuchung der osmotischen Erscheinung" (Magisterial dissertation in Russian), 66 pp., Riga, 1893.
- "Handbuch der Stereochemie," Frankfurt a/M. 1894, [3] + 16 + 1060 pp., ill., 1 port., 8vo. (In collaboration with Carl Adam Bischoff.)
- "Louis Pasteur" (biography in Russian), 24 pp., 8vo, Riga, 1896.
- "Materialien zum Studium der optischen Isomerie" (dissertation in Russian), 134 pp., 8vo, St. Petersburg, 1898.
- "Wilhelm Ostwald," vii + 120 pp., post., 8vo, Leipzig, 1903.

TRANSLATIONS INTO RUSSIAN

- W. OSTWALD: "Wissenschaftliche Grundlagen der analytischen Chemie, 160 pp., Riga, 1896; "Ueberwindung des wissenschaftlichen Materialismus," 26 pp., 8vo, Riga, 1896; "Tabellen zur qualitativen Analyse," 24 pp., 8vo, Riga, 1897.
- E. FISCHER: "Anleitung zur Darstellung organischer Präparate," 83 pp., Riga, 1897.
- J. H. VAN'T HOFF: "Acht Vorträge über physikalische Chemie," 87 pp., 8vo, 1903.
- Development and Activity of the Chemical Laboratory at the Riga Polytechnicum (in Russian), 12 pp., 8vo, Moscow (from the "Lomonossowskij Sbornik").

ARTICLES IN PERIODICALS

Berichte der deutschen chemischen Gesellschaft:

- "Isomerieverhältnisse in der Stilbengruppe" (with A. Kernbaum) 4 pp., Vol. xxiii, 1890.
- "Tetrinsäure, Oxytetrinsäure und ihre Homologie," 14 pp., Vol. xxiv, 1891.
- "Vermeintliche optische Aktivität der Chloralsäure, und über optische-actives Halogenbersteinsäure," 5 pp., Vol. xxvi, 1893.
- "Ricinolsäure und Derivative," 8 pp., Vol. xxvii, 1894.
- "Optisch-actives Hologenverbindungen," 10 and 7 pp., Vol. xxviii, 1895.
- "Gegenseitige Umwandlungen optischen Antipoden," 47 pp., Vols. xxix, xxx, and xxxii.
- "Charakteristik optisch-isomerer Verbindungen," 16 pp., Vol. xxix, 1896.

- Vol. xxx, 1897. "Krystallform optisch-activer Körper," 6 pp.
- "Stereoisomerie Chlorbrombersteinsäuren," 6 pp. "Neues, die Drehungsgrösse steigerndes Mittel," 7 pp. "Optischer Verhalten des Tannins," 6 pp.
- Vol. xxxi, 1898. "Auracaliumlösung," 7 pp. "Vermeintliche Identität des Tannins mit der a-Digallussäure," 8 pp.
- Vol. xxxii, 1899. "Spaltung racemischer Verbindungen in ihre activen Bestandteile," 3 pp. "Verhalten der l-Aepfelsäure beim Erhitzen," 15 pp. "Neues, anorganisches ionisierendes Lösungsmittel," 9 pp. "Optische Drehung der Aepfelsäure im freien und gelösten Zustande," 13 pp.
- Vol. xxxiv, 1901; "Basische Eigenschaften des O," 17 pp.
- Vol. xxxv, 1902; "Das mehrwerthige O," 9 pp.; "Basische Eigenschaften des G," 14 pp.; "Nitroaepfelsäure- & Nitrowein-säureester," 8 pp.; Vol. xxxvi, 1903; "Sogenannte Dinitro-wein-säureester," 3 pp.; "Die Ester der Ricinolsäure," 12 pp.

Liebig's "Jahresbericht der Chemie."

"Optische Isomerie," 80 pp., 1896-97.

Lorenz's "Zeitschrift für anorganische Chemie."

"Zusammengesetzte Rhodan- und Cyanverbindungen," 5 pp., Vol. xxxiii, 1900.

"Anorganische Lösungs- & Ionisierungsmittel," 43 pp., Vols. xxv and xxix, 1900, 1902.

"Flüssiges SO₂ als Lösungsmittel" (with M. Centnerszwer), 106 pp., Vol. xxx, 1902.

Meyer, "J. praktische Chemie."

"Einfluss der Elementen auf die optische Activität des Amylalkohols," 4 pp., Vol. lix, 1899.

Ostwald, "Zeitschrift für physikalische Chemie."

"Bestimmung der Molekulargrößen von Salzen aus der elektrischen Leitfähigkeit ihrer wässrigen Lösungen," 50 pp., Vol. I and II, 1887, 1888.

"Affinitätsgrößen organischer Säuren und ihre Beziehung z. Constitut," 71 pp., Vol. viii, 1891.

Vol. x, 1892, "Tricarbonsäuren," 17 pp.; "Monocarbonsäuren," 27 pp.; "Diffusionserscheinungen und Niederschlagsmembranen," 34 pp.

Vol. xv, 1894, "Optische Drehungen der Ionen," 13 pp.; "Optische Drehungen einiger Derivate des activen Amylalkohols," 28 pp.

Vol. xvii, 1895, "Optisch-actives Derivate der Bernsteinsäure," 22 pp.; "Idem, der Phenyllessigsäure und Optische Superposition," 20 pp.

Vol. xx, 1895, "Optische Drehungen stereoisomerer Verbindungen," 12 pp.; "Einfluss der Bindung auf das optische Drehungsvermögen," 17 pp. "Flüssiges Schwefeldioxyd als Lösungsmittel" (also in Bulletin de l'Académie Impériale des Sciences de St. Petersburg, Vol. xv, No. I, 1901), with M. Centnerszwer, 84 pp., Vol. xxxix, 1902. "Verbindungen des Schwefeldioxyds mit Salzen" (with M. Centnerszwer), 37 pp., Vol. xlii, 1903.

"Ueber abnorme Elektrolyte," Z. physik. Chem., Vol. xliii, pp. 385-464, Leipzig, 1903.

"Ueber organische Lösungs- und Ionisierungsmittel," Pt. I, Z. physik. Chem., Vol. xlvii, pp. 103-188; Leipzig, 1903; Pt. II: "Messungen der elektrischen Leitfähigkeit," op. cit., Vol. liv, pp. 129-230, 1906; Pt. III: "Innere Reibung und deren Zusammenhang mit dem Leitvermögen," op. cit., Vol. lv, pp. 207-249; Pt. IV: "Ebullioscopische Messungen," op. cit., Vol. lv, pp. 281-302; Pt. V: "Lösungsvermögen," op. cit., Vol. lv, pp. 683-720; Pt. VI: "Lösungswärmen," op. cit., Vol. lviii, pp. 479-511, 1907; Pt. VII: "Lösungs- und Dissociationswärmen," op. cit., Vol. lix, pp. 192-211, 1907; Pt. VIII: "Lichtbrechungsvermögen und elektrolytische Dissociation," op. cit., Vol. lix, pp. 385-415; Pt. IX: "Elektrostriktion," op. cit., Vol. lx, pp. 87-100; Pt. X: "Lösende Kraft und Dielektrizitätskonstante," op. cit., Vol. lxi, pp. 633-639, 1908.

"Ueber abnorme Elektrolyte," Z. physik. Chem., Vol. xliii, pp. 385-464, Leipzig, 1903.

"Ausdehnungsmodulus, spezifische Kohäsion, Oberflächenspannung und Molekulargröße der Lösungsmittel," Z. physik. Chem., Vol. lxxv, pp. 129-225, Leipzig, 1908.

"Ueber den Zusammenhang der Kapillaritätskonstanten mit der latenten Verdampfungswärme der Lösungsmittel," Z. physik. Chem., Vol. lv, pp. 257-288, Leipzig, 1909.

"Beiträge zur Kenntnis der Dielektrizitätskonstanten von Lösungsmitteln," Z. physik. Chem., Vol. lxx, pp. 569-619, Leipzig, 1910.

"Ueber die elektrolytische Leitfähigkeiten nichtwässriger Lösungen bei tiefen Temperaturen," Z. physik. Chem., Vol. lxxiii, pp. 257-268, Leipzig, 1910.

"Ueber einige abnorme Temperaturkoeffizienten der molekularen Oberflächenenergie," Z. physik. Chem., Vol. lxxv, pp. 555-577, Leipzig, 1910.

(With R. Swinne) "Beiträge zur Kenntniss der Kapillaritätskon-

stanten von flüssigen Estern." *Z. physik. Chem.*, Vol. XXXIX, pp. 709-738, Leipzig, 1912.

Riga. "Correspondenzblatt," *Journal of the "Naturforscher-Verein,"* Jubilee Volume, 1898.

"Elektrochemie in der Technik," 16 pp.

Sklarski, "Naturwissenschaftliche Rundschau."

"Fünfundzwanzig Jahre Stereochemischer Forschungen," 16 pp.,

Vol. xx, 1900, St. Petersburg.

"Zhurnal Russkogo Fiziko-Khimicheskogo Obshchestva" (*Journal of the Russian Physical-Chemical Society*).

"Vergleichende Untersuchung der Reactionen welche zur Entdeckung der Salpetersäure vorgeschlagen sind," 13 pp., Vol. XIX, 1887.

"Constitution von Demargay's Säuren," 20 pp., Vol. xxiii, 1891.

"Resultate der Untersuchungen der Derivaten von mono- und disubstit. α -Oxysäuren" (with C. A. Bischoff), 15 pp., Vol. xxvi, 1894.

"Optische Isomerie," I: "Active Derivate der Chlorfumaräure und das Drehungsvermögen des Tannins," 20 pp. 11:

"Optische Activität der Halogenverbindungen," 43 pp. 111

"Method der Umwandlung optischer Antipoden," 34

pp. IV: "Hypothese von Ph. A. Guye," 28 pp., Vol. xxx, 1898.

"Ueber anorganische Lösungen und Ionisierungsmittel," *Z. anorg. Chem.*, Vol. xxix, pp. 371-395, Hamburg, 1902.

"Ciekly dwutlenik slarki jako rozpuszczalnik" (Sur l'anhydride sulfureux et son action comme dissolvant). *Wiadomosci matematyczne* (*Gazette of Mathematics*), Vol. vi, pp. 213-243, Warszawa, 1902.

"Flüssiges Schwefeldioxyd als Lösungsmittel," *Z. anorg. Chem.*, Vol. xxix, pp. 513-596; Vol. xxx, pp. 145-250, Hamburg, 1902.

"Ueber das Drehungsvermögen optisch-activer Körper" (address), *Deutsche chem. Ges.*, Vol. xxxiii, pp. 345-409, Berlin, 1905.

"Zusammenhang zwischen der inneren Reibung und Ionengeschwindigkeit, bezw. Diffusionsgeschwindigkeit," *Z. Elektrochem.*, Vol. xii, pp. 77-78, Halle, 1906.

"Ueber das Drehungsvermögen in Lösungen," *Deutsche chem. Ges.*, Vol. xl, pp. 2463-2491, Berlin, 1907.

"Ueber das Wesen des Lösungsvorganges und die Rolle des Mediums," *Rev. Sci.*, Vol. ii, pp. 256-278, Bologna, 1907.

"Ueber die Schmelzwärme, spezifische Kohäsion und Molekulargröße bei der Schmelztemperatur," *Z. Elektrochem.*, Vol. xiv, pp. 713-724, Halle, 1908.

"Zur Geschichte der kolloiden Kieselsäure," *Z. Kolloide*, Vol. vi, pp. 233-235, Dresden, 1910.

"Einige Molekulargrößen in Phosphoroxchlorid als kyroskopischen Solvents," *Z. anorg. Chem.*, Vol. lxviii, pp. 307-316, 1910.

"Die Lösungstheorien in ihrer geschichtlichen Aufeinanderfolge," *Samm. chem.-u. chem. tech. Vorträge*, Stuttgart, 1910, Vol. xv, No. 8/12, pp. 277-454, 8vo.

(With C. A. Bischoff.) "Bisubstit. Bernsteinsäure," *Deutsche chem. Ges.*, 6, 4 and 1 pp., Vol. xxii, 1889.

Physikal. Const. d. substit. Aethenyltricarbonsäureester, 5 pp.; Leitverm. d. substit. Bernsteinsäuren und Glutarsäuren, 8 pp.

Deutsche chem. Ges., Vol. xxiii, 1890.

Glycolid und seine Homologen, 4 pp.; Anwendung d. dynam. Hypothese auf Ketonsäurederivate, 9 pp.; *Deutsche chem. Ges.*, Vol. xxvi, 1893.

Anomalien bei Verkettungen, 4 pp.; Aethylenester d. Glycol- und Oxalsäure und d. Anhydride α -halogenisirter Fettsäuren, 13 pp.; *Deutsche chem. Ges.*, Vol. xxvii, 1894.

Deriv. d. Glycolsäure, 26 pp.; Idem d. Milchsäure, 29 pp.; Idem d. Aepfelsäure, 8 pp.; Idem d. Weinsäure, 15 pp.; Die 1- und 2-bas. α -Oxysäuren, 35 pp.; Liebigs *Jahresber. d. Chem.*, 1894.

A LIST OF UNITED STATES PUBLIC DOCUMENTS PERTAINING TO PULP AND PAPER

The remarkable development of the pulp and paper industry within comparatively recent years has attracted considerable attention, and there is an increasing demand for specific and detailed information in regard to the technical, commercial, and economic features. Much information of this character can be obtained from the public documents or reports of the United States Government, a number of which are specifically devoted to pulp and paper subjects. These particular publications, however, have not been of the greatest usefulness, due, first, to their having been issued at various odd times and by many different branches of the government and, second, to the fact that there was no special catalogue or index bringing them all together for ready reference. On this account, the list of titles below will be found of much advantage.

The publications listed vary widely in subject matter, depending on the character of the investigations conducted by the different branches of the government by which the reports were issued. However, these investigations do not cover every feature of the pulp and paper industry so it must not be expected that all desired information can be obtained from government publications. For the particular subjects considered the reports are quite thorough since the scope of government investigations usually is far greater than could be attained by independent investigators.

Aside from being readily accessible in many public libraries, most of these publications may be secured by purchase from the Superintendent of Documents, Government Printing Office, Washington, D. C., at very small cost. Many of them also are available for gratuitous distribution by Members of the Senate or House of Representatives and by the respective Departments and Bureaus from which they were issued. The ease with which they may be obtained, combined with their authoritative and impartial nature, renders them especially valuable as sources of information.

It is believed that with the following exceptions the list contains the titles of all government publications pertaining more or less directly to pulp and paper subjects. The principal exceptions are the decisions and reports of the Interstate Commerce Commission and the Monthly Consular and Trade Reports of the Bureau of Manufacturers (later the Daily Consular and Trade Reports of the Bureau of Foreign and Domestic Commerce) of the Department of Commerce and Labor. The former often have reference to particular cases before the Commission in which pulp and paper figure merely as articles of shipment, and the points at issue are such as freight classification, tariff rates, shortage of cars, and similar transportation subjects. The Consular and Trade Reports frequently contain short articles by American Consuls dealing with paper products in foreign countries, together with suggestions for home manufacturers. The Geological Survey of the Department of the Interior and the two Statistics Bureaus of the Departments of Agriculture and of Commerce and Labor have each published certain information (other than that indicated in the list below) on subjects relating to pulp and paper-making but this has generally been included in reports in a form not particularly applicable to this industry alone.

The branches of the government from which the several publications were issued are indicated in the headings.

AGRICULTURE DEPARTMENT

BRAND, CHARLES J. The Utilization of Crop Plants in Papermaking. 12 pp., illus. 8°. 1911. (Dept. Agr., yrbk., separate, 1910.)

DODGE, CHAS. RICHARDS. A Descriptive Catalogue of Useful Fiber Plants of the World; Including the Structural and Economic Classification of Fibers. With appendices. 361 pp., 103 fig., 13 pl., tables. 8°. 1897. (Dept. Agr., Fiber Inv., Rpt. 9—out of print.)

DODGE, J. R. Maize Paper and Maize Cloth. 3 pp. 8°. 1863. (In: Dept. Agr., yrbk., 1863.)

VEITCH, F. P. Suitable Paper for Permanent Records. 6 pp. 8°. 1909. (Dept. Agr., yrbk., separate, 1908—out of print.)

WILEY, H. W. and C. H. MERRIAM. Durability and Economy in Papers for Permanent Records. A report submitted by H. W. Wiley and C. Hart Merriam, Committee on Paper for Departmental Use. Including paper specifications, by F. P. Veitch. 51 pp., illus. 8°. 1909. (Dept. Agr., Rpt. 89.)

CHEMISTRY BUREAU

CHEMISTRY BUREAU. Examination of Paper. 10 pp., 2 tables. 8°. 1907. (Dept. Agr., Bur. Chem., Circ. 34.)

HAYWOOD, J. K. Arsenic in Papers and Fabrics, by J. K. Haywood, with the collaboration of H. J. Warner. 53 pp., 13 tables. 8°. 1904. (Dept. Agr., Bur. Chem., Bull. 86.)

SAMMET, C. FRANK. A Measurement of the Translucency of Papers. 3 pp., table. 8°. 1912. (Dept. Agr., Bur. Chem., Circ. 96.)

SAMMET, C. FRANK. Detection of Faulty Sizing in High-grade Papers. 3 pp., 3 pl. 8°. 1913. (Dept. Agr., Bur. Chem., Circ. 107.)

VEITCH, F. P. Papermaking Materials and their Conservation. 23 pp., tables. 8°. 1909. (Dept. Agr., Bur. Chem., Circ. 41.)

VEITCH, F. P. and J. L. MERRILL. Pulp and Paper and other Products

from Waste Resinous Woods. 28 pp., 11 tables. 8°. 1913. (Dept. Agr., Bur. Chem., *Bull.* 159.)

FOREST SERVICE

FOREST SERVICE. See Commerce and Labor Department, Census Bureau.
FOX, WILLIAM F. A History of the Lumber Industry in the State of New York. 59 pp., illus. 8°. 1902. (Dept. Agr., Bur. For., *Bull.* 34.) Contents (in part): Methods of lumbering, transportation of pulpwood, wood pulp.

GRAVES, HENRY S. and E. A. ZIEGLER. The Woodsman's Handbook. Rev. and enl. ed., with appendix. 208 pp., 83 tables, 16 fig. 12°. 1910. (Dept. Agr., For. Serv., *Bull.* 36.) Contents (in part): Measurement of timber; growth and volume tables for woods used in pulpmaking.

HALE, H. M. See Commerce and Labor Department, Census Bureau.

KELLOGG, R. S. The Timber Supply of the United States. 24 pp., 6 tables. 8°. 1909. (Dept. Agr., For. Serv., *Circ.* 166.)

MAXWELL, HU and H. S. SACKETT. Wooden and Fiber Boxes. 14 pp. 8°. 1911. (Dept. Agr., For. Serv., *Circ.* 177.)

SURFACE, HENRY E. Paper Pulp from Various Forest Woods; Experimental Data and Specimens of Soda and Sulfite Pulp. 29 + 55 pp., 4 tables. 12°. 1912. (Dept. Agr., For. Serv., unnumbered bull., For. Prod. Lab. series.)

SURFACE, HENRY E. Bibliography of the Pulp and Paper Industries. 48 pp. 8°. 1913. (Dept. Agr., For. Serv., *Bull.* 123, For. Prod. Lab. series.)

SURFACE, HENRY E. The Effects of Varying Certain Cooking Conditions in the Production of Soda Pulp from Aspen. 75(?) pp., 17 tables, 8 pl., 20 text fig. 8°. 1913. (Dept. Agr., For. Serv., *Bull.* For. Prod. Lab. series—in press.)

THICKENS, J. H. Experiments with Jack Pine and Hemlock for Mechanical Pulp. 29 pp., 10 tables, 15 pl. Specimens of papers. 8°. 1912. (Dept. Agr., For. Serv., unnumbered bull., For. Prod. Lab. series.)

THICKENS, J. H. The Grinding of Spruce for Mechanical Pulp. 40(?) pp., 6 pl., 19 text fig. 8°. 1913. (Dept. Agr., For. Serv., *Bull.* 127, For. Prod. Lab. series—in press.)

WEIGLE, W. G. and E. H. FROTHINGHAM. The Aspens; their Growth and Management. With appendix. 35 pp., 10 tables. 8°. 1911. (Dept. Agr., For. Serv., *Bull.* 93.)

PLANT INDUSTRY BUREAU

BRAND, CHARLES J. Crop Plants for Papermaking. Printed on papers made from various annual plants. 19 pp., 3 fig. 8°. 1911. (Dept. Agr., Bur. Plant Ind., *Circ.* 82.)

FAIRCHILD, DAVID G. Three New Plant Introductions from Japan. 22 pp., 6 pl. 8°. 1903. (Dept. Agr., Bur. Plant Ind., *Bull.* 42.) Contents (in part): Mitsumata, a Japanese paper plant, pp. 9-17.

CONGRESS

PRINTING JOINT COMMITTEE. Report of Committee on Paper Specifications to the Joint Committee on Printing in Compliance with its Resolution of August 15, 1911. December 18, 1911. 37 pp., tables. 8°. 1911.

PUBLIC LAWS—TARIFF. The Tariff Act of 1909. An act to provide revenue, equalize duties and encourage the industries of the United States and for other purposes. Approved August 5, 1909. 158 pp., index. 8°. 1909. (H. R. 1438, public No. 5.) Contents (in part) consist of specific information on the customs, duties, and regulations affecting the importation of papermakers' raw materials and intermediate and finished products.

HOUSE OF REPRESENTATIVES

MANN, J. R. Report from Select Committee on Pulp and Paper Investigation under H. Res. 344; with Views of Minority. 18 pp. 8°. May 12, 1908. (H. rp. 1786, 60th Cong., 1st sess.)

MANN, J. R. Report from Select Committee on Pulp and Paper Investigation. 7 pp. 8°. February 15, 1909. (H. rp. 2206, 60th Cong., 2nd sess.) Consists of a brief survey of the industry from various viewpoints.

PULP AND PAPER INVESTIGATION SELECT COMMITTEE. Pulp and Paper Investigation Hearings. April 25, 1908.—February 19, 1909. 6 vols. 235 + 3366 pp., tables. Index. 8°. 1908-1909. (H. doc. 1502, 60th Cong., 2nd sess.)

WAYS AND MEANS COMMITTEE. Tariff Hearings. . . . 1896-1897. Vol. II pp. 1751-1798. Schedule M—Pulp, papers, and books. 8°. 1897. (H. doc. 338, 54th Cong., 2nd sess.)

WAYS AND MEANS COMMITTEE. Tariff Hearings. . . . 1908-1909. Vol. VI, pp. 5879-6389. Schedule M—Pulp, papers, and books. Tables. 8°. 1909. (H. doc. 1505, 60th Cong., 2nd sess.)

SENATE

FINANCE COMMITTEE. Replies to Tariff Inquiries. Schedule M—Pulp, papers, and books. 104 pp., tables. 8°. 1894. (S. rp. 513, Pt. 2-3, 53rd Cong., 2nd sess.)

LODGE. Laws Enacted in Nova Scotia, Ontario, British Columbia, Quebec, and New Brunswick, Canada, Relative to Spruce and other Pulpwoods Cut on Crown Lands. 5 pp. 8°. May 15, 1911. (S. doc. 28, 62nd Cong., 1st sess.)

NATIONAL CONSERVATION COMMISSION. Report of Commission, February 1909. Special message from President of the United States transmitting report of commission, with accompanying papers; edited by Henry Gannett. 3 vol., illus., tables, maps. 8°. 1909. (S. doc. 676, 60th Cong., 2nd sess.) Contents (in part): Vol. II includes discussions of timber stands, growth, wastes and utilization by chemical and other means.

TARIFF BOARD. Reciprocity with Canada. Message from the President of the United States transmitting in response to Senate Resolution of February 23, 1911, a report from the Tariff Board relative to various commodities named in the proposed Canadian reciprocity measure. 131 pp., tables. 8°. 1911. (S. doc. 849, 61st Cong., 3rd sess.) Contents (in part): Pulp and newsprint paper, pp. 7-82.

TARIFF BOARD. Pulp and Newsprint Industry. Message from the President of the United States transmitting a report by the Tariff Board, relative to pulp and newsprint industry. 134 pp., 87 tables. Diag. 8°. 1911. (S. doc. 31, 62nd Cong., 1st sess.)

COMMERCE AND LABOR DEPARTMENT

CENSUS BUREAU. Pulpwood Consumption. Annual 1905-1910. About 12 pp. each, tables. 8°. 1906-1911. Appears also in *its* Forest products of the United States. 1905 comp. by H. M. Hale for the Forest Service, U. S. Dept. of Agriculture; 1906-1910, comp. by the Bureau of the Census and the Forest Service, in cooperation; 1905-'06, published as *Circ.* 44, 120 of the Forest Service; 1907-'10 published by the Bureau of the Census as Forest Products No. 1. Title varies: 1905. Wood Used for Pulp; 1906. Consumption of Pulpwood.

CENSUS BUREAU. Paper and Wood Pulp. 43 pp., 19 tables. 4°. 1907. (Dept. Com. and Lab., Bur. Census, 1905 Census of Manufactures, *Bull.* 80.)

CENSUS BUREAU. Paper and Wood Pulp Statistics; preliminary report for 1909, issued April 26, 1911. 6 pp., tables. 8°. 1911. (Dept. Com. and Lab., Bur. Census circ.)

CENSUS BUREAU. See Interior Department, Census Office for earlier census publications.

LABOR DEPARTMENT. The Production of Paper and Pulp in the United States from January 1 to June 30, 1898. Tables. 8°. July, 1899. (In: Dept. Labor, *Bull.* 23, pp. 546-549.)

INTERIOR DEPARTMENT

CENSUS OFFICE

CENSUS OF 1860. Manufactures of the United States in 1860. 217 + 745 pp., tables. 4°. 1865. (Dept. Int., Census Off., 8th census rpt.) Contents (in part): Paper and paper-hangings, history and statistics, pp. cxxi-cxxxii.

CENSUS OF 1870. The Statistics of the Wealth and Industry of the United States. . . . Ninth Census (June 1, 1870). 831 pp., tables. 4°. 1872. (Dept. Int., Census Off., 9th census rpt.) Contents (in part): Specified industries, p. 411, et seq., paper, paper-hangings, paper bags, paper boxes.

CENSUS OF 1880. Report on the Forests of North America (exclusive of Mexico), by Charles S. Sargent. 612 pp., 3 Pts., maps. Index. 4°. 1884. (Dept. Int., Census Off., 10th census rpt., Vol. IX.) Contents (in part): Chemical, physical and mechanical properties of woods.

CENSUS OF 1880. Report on the Manufactures of the United States at the Tenth Census (June 1, 1880) Embracing General Statistics. 476 pp., tables. 4°. 1883. (Dept. Int., Census Off., 10th census rpt., Vol. 2, Manufactures.) Contents (in part): Statistics, by States, on wood pulp, paper and paper-hangings, envelopes, leather-board, cardboard, etc.

CENSUS OF 1880. The Newspaper and Periodical Press, by S. N. D. North. 446 pp., tables. 4°. 1884. (Dept. Int., Census Off., 10th census rpt., Vol. VIII.)

CENSUS OF 1890. Report on Manufacturing Industries in the United States at the Eleventh Census (1890), by William M. Stewart and others. Tables. 4°. 1895. (Dept. Int., Census Off., 11th census rpt., Mfg. ind., Pts. I and III.) Contents (in part): Part I. Totals, by different branches of the paper industry, p. 62; comparative statements regarding paper, 10th and 11th censuses, pp. 649-650; detailed statement, regarding paper, by states, pp. 722-723. Part III. Forest industries—wood pulp.

CENSUS OF 1900. Manufactures Part III. Special reports on selected industries, by S. N. D. North and others. 4th ed., 1140 pp., tables. 4°. 1906. (Dept. Int., Census Off., 12th census rpt., Vol. IX, Pt. III.) Contents (in part): The Lumber Industry, by Henry Gannett, pp. 803-897; Paper and Pulp, by Charles W. Rantoul, Jr., pp. 1013-1035; Printing and Publishing (including kind, cost, and quantity of paper used), by William S. Rossiter, pp. 1037-1139.

CENSUS OF 1900. Manufactures: Paper and Pulp, by S. N. D. North and Charles W. Rantoul, Jr. 13 pp., 4 tables. 4°. Issued Sept. 30, 1901. (Dept. Int., Census Off., 12th census, *Bull.* 99.)

LATER CENSUSES. See Commerce and Labor Department, Census Bureau.

GEOLOGICAL SURVEY

LEIGHTON, MARSHALL ORA. Preliminary report on the Pollution of Lake

- Champlain. 119 pp., 33 tables, 13 pl., 5 fig., maps. Index. 8°. 1908. (Dept. Int., Geol. Surv., w. s. and i. p. 121.)
- PARKER, HORATIO N. and others. The Potomac River Basin. 364 pp., 8 pl., tables, maps. Index. 8°. 1907. (Dept. Int., Geol. Surv., w. s. and i. p. 192.) Contents (in part): Stream pollution—wood pulp, by Horatio N. Parker, p. 201; Effects of some industrial wastes (paper and pulp mill) on fishes, by M. C. Marsh, p. 340.
- PHILIPS, EARLE BERNARD. The Prevention of Stream Pollution by Straw-board Waste. 29 pp., 2 fig., 2 pl., tables. 8°. 1906. (Dept. Int., Geol. Surv., w. s. and i. p. 189.)
- PHILIPS, EARLE BERNARD. The Pollution of Streams by Sulfite Pulp Waste. A Study of Possible Remedies. 36 pp., tables. 8°. 1909. (Dept. Int., Geol. Surv., w. s. p. 236.)
- SACKETT, ROBERT LEMUEL and ISAIAH BOWMAN. The Disposal of Straw-board and Oil-weld Wastes. 52 pp., 4 pl., tables, maps. Index. 8°. 1905. (Dept. Int., Geol. Surv., w. s. and i. p. 113.)

STATE DEPARTMENT

- FOREIGN COMMERCE, BUREAU OF. Paper in Foreign Countries; Uses of Wood Pulp. 533 pp., tables. Index. 8°. 1900. (Dept. State, Bur. For. Com., spl. cons. rpt., Vol. XIX.)
- SILCOX, GEORGE W. Report on the Art of Printing and on Manufactures of Paper at the International Exhibition Held at Vienna, 1873. With appendix. 30 pp. Index. 8°. 1875. (Dept. State, U. S. Com. Vienna Int. Exh. 1873, rpt., sect. O, Vol. II.) Contents (in part): Chapter IV, Manufacture of Paper; appendix, Manufacture of Paper Barrels.

TREASURY DEPARTMENT

- TREASURY DECISIONS. No. 31772 (Treas. Dept., Circ. 48, 1911). Reciprocity between the United States and Canada, July 26, 1911; No. 31783, Wood Pulp—Printing Paper, July 29, 1911; No. 31890, Wood Pulp—Paper, September 29, 1911; No. 32238, Wood Pulp—Printing Paper, February 12, 1912; No. 32757, Wood Pulp—Paper and Paper Board, August 10, 1912. Leaflets. These decisions together with the Tariff Act of 1909 (see *Congress—Public Laws—Tariff—H. R. 1438*)

constitute the customs regulations (in effect November, 1911), pertaining to the importation of pulp-wood, wood pulp and paper.

The author would appreciate having his attention called to any omissions or errors in the above list

HENRY E. SURFACE.

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN
FEBRUARY 1, 1913

AMERICAN CHEMICAL SOCIETY—NEW DESCRIPTIVE DIRECTORY OF THE DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS

It is desired to issue a new descriptive directory of the Division of Industrial Chemists and Chemical Engineers in December, 1913. In order to do this the members of the division are requested to notify the secretary of changes of address, occupation, etc., and to contribute one dollar each toward the expenses of the division. It is absolutely necessary that the list of members should be corrected and brought up-to-date and it is hoped that each member will attend to this immediately.

Any other member of the Society wishing to enroll in the Division should send his name, address, occupation (title and business connection) and lines in which he is most interested to the Secretary, together with one dollar as a contribution toward the expenses of the division.

S. H. SALISBURY, JR., Secretary

LEHIGH UNIVERSITY,
SOUTH BETHLEHEM, PA.

OBITUARIES

WILLIAM McMURTRIE

In September, 1872, I left my home in Indiana for the purpose of taking a post-graduate course at Harvard University. Never having been in the National Capitol, I took occasion to visit Washington en route. At that time Dr. R. T. Brown, one of the old-fashioned scientists who had been professor of chemistry in the medical college which I attended, was chemist of the Department of Agriculture. I visited the Department for the purpose of paying him a friendly call. On entering the laboratory, I found one assistant at work: a young man with jet-black hair and pleasing appearance, seated on a high stool, before a desk, attending to some of the details of an analysis. On inquiring of him for my friend, Dr. Brown, I was told that he was not in, and the young man introduced himself as William McMurtie, assistant. This was my first meeting with Dr. McMurtie, and the beginning of a friendship which continued unabated until the time of his death. The impression made upon me by Dr. McMurtie at that time is indelible. The picture which I have just described is as vividly before me now as it was forty-one years ago.

Dr. McMurtie's career in the Department of Agriculture was signalized by the usual activity which he always displayed in every position that he filled. Within the next two years from the time of which I speak, Dr. Brown retired from the position of the chief chemist of the Department of Agriculture and Dr. McMurtie took his place. He was at that time, though only twenty-one years of age, well trained in chemistry, as training was regarded in those days. It is stated that even in his boyhood he displayed a remarkable liking for chemistry. At the age of fourteen he attended some lectures given to young people by the minister of the neighborhood and gladly paid the fee of five cents which was necessary to cover the costs of the materials for each of the lectures. When he entered Lafayette College there was no special course of chemistry, so he took mining engineering because in that he could have the best chemical training which the college afforded.

The story of how he was selected for the succession to Dr. Brown reveals one of the characteristics of his whole life, namely, unselfishness. Judge Watts was at the time Commissioner of Agriculture. When Dr. Brown retired, a number of applications for this position came in. Commissioner Watts called young McMurtie into his office and asked him what he thought of the qualifications of the applicants. He said that he did not think any one of them was properly qualified for the position. Commissioner Watts then asked him if he thought he could do the work and would like the position. He replied that the idea of succeeding Dr. Brown had never entered his mind, but he thought he could do better than any of the men who were being considered. The Commissioner replied: "You have not made any application." It was not long, however, before the application was made out and he continued to hold the position of Chief Chemist until 1877.

The story of his retirement from this position is most interesting. During the term of President Hayes, Mr. Le Duc was Commissioner of Agriculture. He evidently had some political debts to pay, for among other things he wanted Dr. McMurtie's place for Dr. Collier. Commissioner Le Duc had a very fine opinion of Dr. McMurtie's ability and services and frankly told him the predicament he was in and asked if he could give him something else, would he be willing to step aside. With his well-known devotion to others Dr. McMurtie readily consented. He retired from the position of Chief Chemist of the Department and went to Paris in 1878 as a representative of the Department of Agriculture. In addition to discharging his special duties as representative of the Department he made a thorough and extensive study of the beet industry and of the wine industry of France. His report on the sugar industry laid the foundation of the scientific beet sugar industry of this country and is one of the most valuable contributions Dr. McMurtie made to science.

After his return from Europe, he continued his relations with the Department and carried on a very elaborate investigation

on the subject of fibers, especially of wool and cotton. He continued these investigations after he accepted the position of Professor of Chemistry in the University of Illinois. It was my good fortune to know something of the details of his fine work. It was a work of monumental proportions and carried out with all the devotion to detail which Dr. McMurtrie brought to the study of every problem. His microscopical and physical study of fibers occupied much of his time and that of several assistants, whom he employed for a number of years. For some reason the valuable manuscripts which he prepared for the Department of Agriculture have never been published in full. It would be a great tribute to his memory as well as of great value to science if these unpublished manuscripts could be made public.

Dr. McMurtrie discharged his pedagogical duties with distinction and at the same time kept up his laboratory studies.

An investigation into an alleged case of poisoning by baking powder led to his coming into contact with the officials of the Royal Baking Powder Company; in 1888, he resigned his chair of chemistry in the University of Illinois, and became consulting chemist of that company. He continued his connection with that company first as chemist, then as manager and later as vice-president, until the time of his death.

My most intimate association with Dr. McMurtrie in an official way, was in the reorganization of the American Chemical Society. We were members of the committee which formed the present constitution and made possible the useful activity of the society. In the early nineties, the American Chemical Society numbered scarcely more than two or three hundred members. The journal was a matter of no consequence and the meetings were confined to New York City. The committee on reorganization realized that the only avenue of prosperity lay in the direction of popularizing and localizing the activities of the society. The plan of forming local sections appealed to the committee as the only solution of this difficult problem. To this plan Dr. McMurtrie devoted his services with his customary zeal and enthusiasm. The wisdom of the reorganization is apparent at the present time. There are 42 local sections scattered throughout the country and a total membership of around 6,000. Dr. McMurtrie's services in this line were recognized by his fellow chemists, in his election as president of the society in 1896-8, the duties of which position he discharged with great credit to himself and benefit to the society.

Dr. McMurtrie's later years were devoted to executive rather than laboratory work, and for this reason the number of his contributions to scientific literature in later life was not numerous. In spite of this, however, his love of his chosen profession

never waned. In the three years prior to his death, in which he was an invalid, he manifested a most lively interest in all things relating to the prosperity of the American Chemical Society and the advancement of chemistry. Not only was he an extensive reader of chemical literature during these three years of invalidism, but he carried on a most extensive correspondence with his old friends and new ones in matters relating to chemistry. He will be known professionally to the succeeding generations by his contributions to agricultural chemistry, most especially his work in laying broad and deep the foundations of the sugar beet industry of this country. His great work on fibers is known to only a few of his intimate friends. In his connection with a great manufacturing company, he, doubtless, was restricted to some extent in his publications by the code of ethics governing such positions. While this code is to be regretted from a scientific point of view, it is probably the only one which could exist in the present condition of commercial operations.

In his relations to his fellow workers, Dr. McMurtrie was the ideal *persona grata*. His wit, his humor and his geniality illuminated every function he attended. He died peacefully on the 24th of May, 1913, as the victim of apoplexy, his arteries having hardened altogether too early, largely perhaps by reason of devotion to his profession.

Friend, counsellor, co-laborer, *vale*.

HARVEY W. WILEY

BIOGRAPHICAL DATA

WILLIAM MCMURTREE

Born March 10, 1851, near Belvidere, New Jersey.

Degree, M.E., Lafayette College, 1871.

Degree, M.S., Lafayette College, 1874.

Degree, Ph.D., Lafayette College, 1876.

Married—Washington, D. C., to Helen Douglas.

His wife and son Douglas C., survive him.

Died—May 24, 1913, result of apoplexy.

Buried—Oak Hill Cemetery, Washington, D. C.

BIBLIOGRAPHY OF SCIENTIFIC WRITINGS BY WILLIAM MCMURTREE

Chemical Memoranda. *United States Department Agriculture Monthly Reports*, 1873-1876.

Address. *United States Department Agriculture, Division of Chemistry, Bulletin 62*, Wash., 1900, pp. 70-72. 17th Annual Convention. Association of Official Agricultural Chemists.

On the Mineral Nutrition of the Vine for the Production of Wine. *United States Department Agriculture, Report No. 22*, pp. 180-187.

Report on the Culture of Sumac in Sicily and its Preparation for Market in Europe and the United States. *United States*



DR. WILLIAM MCMURTREE

Department Agriculture, *Special Report* No. 26, Vol. II, 1879-80, Wash., 1880.

Report on the Culture of the Sugar Beet and the Manufacture of Sugar therefrom in France and the United States. United States Department Agriculture, *Special Report* No. 28, Vol. II, 1879-80, Wash., 1880.

Report on the Examination of Raw Silks. United States Department Agriculture, Division of Entomology, *Bulletin* 3, pp. 56-71, Wash., 1883.

Report upon an Examination of Wools and Other Animal Fibers. Washington, 1886, 613 pp., 34 charts, 38 pl. Quarto. United States Department Agriculture. Also in United States 49th Congress, 1st Session, House Miscellaneous Document 392. Serial No. 2426, Wash., 1886.

Reports upon Statistics of Grape Culture and Wine Production in the United States for 1880. United States Department Agriculture, *Special Report* No. 36, Wash., 1881.

Report of the Chief of the Division of Chemistry. United States Commissioner of Agriculture, *Annual Report*, 1873, pp. 170-183; 1874, pp. 147-155; 1875, pp. 141-151; 1876, pp. 46-61; 1877, pp. 65-89.

Bat Guano. United States Department Agriculture. *Monthly Report*, 1876, p. 192.

Wool—Its Structure and Strength. *Thirteenth Report of the Board of Trustees of the University of Illinois*, pp. 223-54. Springfield, Ill., 1887.

Wools and Other Animal Fibers. In United States World's Columbian Commission, Wash., 1901. World's Columbian Exposition, 1901, Vol. 2, pp. 1519-1690.

Some Records of the Year's Progress in Applied Chemistry.

Journal of the American Chemical Society, Easton, 1898, Vol. 20, pp. 967-987.

Some Records of Progress in Applied Chemistry. *Journal of the American Chemical Society*, Easton, 1899, Vol. 21, pp. 1145-1175.

The Condition, Prospects, and Future Educational Demands of the Chemical Industries. Presidential Address at the Chicago meeting of the American Chemical Society. Portrait. *Journal of the American Chemical Society*, Easton, 1901, Vol. 23, pp. 71-89.

The Education of Technical Chemists. *Chemical Engineer*, Philadelphia, 1905, Vol. 2, pp. 142-143. Abstract in *Review of American Chemical Research*, Easton, 1905, Vol. 11, p. 600.

Address at the Dedication of the Walker Laboratory of the Rensselaer Polytechnic Institute. *Science*, N. S., New York, 1907, Vol. 26, pp. 329-334. Rev. in *Chemical Abstracts*, Easton, 1907, Vol. 1, p. 3042.

Address Delivered at the Inauguration of William A. Noyes as Head of the Department of Chemistry and Director of the Chemical Laboratory at the University of Illinois, October 18, 1907. *Science*, New York, 1907, N. S., Vol. 26, pp. 694-699.

The Chemists' Club. *Science*, New York, 1911, N. S., Vol. 34, pp. 5-7.

Disposal of Sewage with Recovery of Elements of Plant Food for Use in Agriculture. *Journal of Industrial and Engineering Chemistry*, Easton, Vol. 5, p. 156.

NOTE: The above is as complete a list as could be obtained at this writing.—DOUGLAS C. McMURTRIE

NOTES AND CORRESPONDENCE

THE SAMPLING OF RUBBER GOODS¹

Investigations have been made at various times to show the great importance of sampling such material as coal, sugar, alloys of various kinds, etc., and a great deal has been written on this subject, showing that the value of the chemical analysis made depends largely on the care expended in sampling. With regard to the sampling of rubber goods very little has been said, and if we may judge by the experience of this Bureau, little attention has been paid to this important subject. Yet it must receive the most careful consideration from all who are interested in the chemical analysis of rubber, if we are to expect analyses made in different laboratories to reach even fair agreement.

Inasmuch as rubber compounding is merely mechanical mixing of solid material of varying natures, it is obvious that a fair average sample can be obtained only by taking pieces from different parts of the finished material.

As a rule, the matter of sampling is left to a corps of inspectors, to whom rubber is only one of many materials to be handled. Too much must not be expected of them. In such cases, it is always the manufacturers who have most at stake, and it would seem that they are the ones who should insist that the sampling be done properly.

For example, some months ago, this Bureau had occasion to test a sample of suction hose. A small strip was taken from the end of one length, and another sample, one foot in length, was sent by the manufacturer, with the guarantee that it was made of the same material, and vulcanized under the same conditions. The analysis of the inspector's sample showed it to be much inferior to the one submitted by the manufacturer. The material was rejected, and considerable annoyance and expense was caused, until the manufacturer proved that the hose was capped

with a somewhat inferior compound. If the manufacturer, who knew all the conditions, had made this statement at the time the sample was taken, much delay and expense in re-testing would have been saved.

Furthermore, samples should not be subjected to any treatment whatever before they are sent to the testing laboratory. Recently, we received a sample of insulated wire, which, on examination, proved to contain a variety of materials. Part of it was a piece of wire just as it came from the reel, some of it the rubber stripped from the wire, and the largest part material that had been stripped from the wire and worked through a mill, "to give an average sample" as the inspector explained. The rubber on the wire showed a free sulfur content of 0.79 per cent, whereas the specifications allowed only 0.50 per cent. The other material, however, showed a free sulfur content as low as 0.42 per cent. Analysis of samples of this nature is a waste of time and money, since there can be no assurance that the results obtained bear any relation to the material which the contractor is offering.

Still another sample has been received recently, consisting of rubber which had been ground to pass through a No. 20 sieve. This was sent in a paper envelope, not sealed. The absurdity of the analysis of such material is apparent to all who have given any time and thought to the question of the chemical analysis of rubber. Suffice it to say that practically all analytical methods require the analysis to be started within 24 hours after the grinding of the sample.

Care of the sample after taking is equally important. A testing laboratory can analyze a sample only as it is received, and it is to the manufacturer's interests that this sample be received in a satisfactory condition.

This subject should come under the jurisdiction of the rubber section of the American Chemical Society and we would recommend that some action be taken. This Bureau is now insisting

¹ Published by permission of the Director of the Bureau of Standards. Paper presented at the Milwaukee meeting of the American Chemical Society, March, 1913.

that material for analysis should meet the following requirements:

Samples shall be taken directly from the finished material. These samples should be sealed, and marked with maker's name, date of sampling, kind of material, and sufficient other data to ensure easy and complete identification. The sample should be of such size as to permit of part being taken for analysis and the remainder stored for future reference, should the occasion for such arise. Every precaution must be taken to prevent contamination of the samples by any foreign material, and they must always be stored in a cool place. The object of these precautions is to insure that the sample shall be received in exactly the same condition as it is offered by the contractor.

The following table will show the minimum amount of material required for making the various tests, leaving a sufficiency for supplemental chemical check tests if these are needed. The amounts specified are intended to show the size of sample required on what might be considered relatively small lots. The samples should be made up of a number of pieces taken from several parts of the delivery, and from these a composite sample will be made for chemical analysis. It should be noted, however, that the pressure test on hose requires a four-foot length. Large lots should be represented by samples of corresponding size. In such cases, it may be advisable to make two, or more, composite samples for chemical analysis.

PHYSICAL TESTS ONLY

Hose of all kinds, up to 3 in. diameter.....	2 feet
Hose of all kinds, over 3 in. diameter.....	1 foot
Pressure test on hose.....	4 feet
Packing.....	1 sq. ft.
Insulated wire.....	4 to 6 feet
Other mechanical goods,	
sufficient material to give at least 6 pieces 1 in. X 6 in.	

CHEMICAL TESTS ONLY

Hose of all kinds, up to 3 in. diameter.....	1 foot
Hose of all kinds, over 3 in. diameter.....	6 inches
Packing.....	1/4 sq. ft.
Insulated wire.....	2 to 3 feet
Other mechanical goods,	
sufficient material to give at least four ounces of rubber.	

ELECTRICAL TESTS ONLY

Insulated wire.....	6 feet
---------------------	--------

JOHN B. TUTTLE

BUREAU OF STANDARDS
WASHINGTON, D. C.

BAKELITE PATENT RECOGNITION

As a result of negotiations between the General Bakelite Company and the Condensite Company of America, the suits brought by the former against the latter and its customers for alleged infringement of the Bakelite patents, have been withdrawn, and the Condensite Company, recognizing the pioneer character of Dr. L. H. Baekeland's work, has acknowledged the validity of the Bakelite patents in suit and some others, and will pay substantial royalties thereunder.

The General Bakelite Company will continue the manufacture of Bakelite under its numerous patents, and the Condensite Company will manufacture Condensite under the Aylsworth patents, as well as the license just granted for such of the Baekeland patents as are broad enough to cover Condensite.

This recognition of the force and validity of the principal Baekeland patents by the only other manufacturer of condensation products is a confirmation of the Bakelite Company's claims for the broad scope and pioneer character of these patents.

There is much that is old in the art of making phenolic condensation products, but Dr. Baekeland was the first to make practical application of what theretofore had been chiefly laboratory experiments.

NOTE ON THE STANDARD VANILLIN SOLUTION FOR THE COLORIMETRIC METHOD FOR THE DETERMINATION OF VANILLIN IN FLAVORING EXTRACTS

Since the publication in THIS JOURNAL, 4, p. 670, of "A New Colorimetric Method for the Determination of Vanillin in Flavoring Extracts," by Otto Folin and W. Dennis, the method has been used in the Kansas State Board of Health Food Laboratory in the analysis of over sixty extracts and a number of samples of known vanillin content.

The method has worked well and has given sufficiently accurate results for judging vanilla extracts but some experiments with the standard vanillin solution seem important enough to be reported.

The directions call for a solution of vanillin of which 10 cc. contain 0.001 gram of vanillin. Experiments have shown that this solution increases, on standing, in its power to produce a blue color when treated with the phosphotungsticphosphomolybdic acid reagent so that after a month it increases to such an extent that determinations on solutions of vanillin of known strength showed only about 75 per cent of the true vanillin content. Such results are illustrated by the following estimations:

Date	Fresh standard	Old standard
1-18-13.....	20.0	15.4
2-24-13(a).....	0.501	0.356
Duplicate.....	0.498	0.362

(a) This was a solution 0.5000 gram of Merck's refined vanillin (same as used in standard) and 25 cc. of 95 per cent alcohol in 100 cc.

A very satisfactory standard solution may be prepared by dissolving 2.0000 grams of vanillin in 200 cc. of 95 per cent of alcohol and diluting to one liter and then using 10 cc. of this solution to make 200 cc. of standard solution when it is needed. Such a solution was made January 18, 1913, and standards made by diluting the strong solution were compared with fresh standards with the results shown in the following table:

Date	Fresh standard	Standard made by dilution
1-18-13.....	20.0	20.2
1-22-13.....	20.0	20.1
1-25-13.....	20.0	20.3
1-29-13.....	20.0	20.1
3-21-13.....	20.0	20.1

These results show that the strong solution will keep for at least two months without showing an appreciable change. It is much easier to make the dilution than to make up a fresh standard each day.

OSCAR E. HARDER

UNIVERSITY OF KANSAS
LAWRENCE
MAY 16, 1913

DETERMINATION OF SULPHATE IN AMMONIUM SULFATE SOLUTIONS, ETC.—A CORRECTION

Through a clerical error in the paper under the above title, THIS JOURNAL, 5, 469, no reference was made to the paper published by H. F. Muer, "The Determination of Sulfur in Coal by Means of the Jackson Turbidimeter," THIS JOURNAL, 3, 553. Muer's paper was carefully consulted in connection with our work, and the reference made to it on the original manuscript was omitted by a clerical error in the Bureau offices. The apparent discrepancies in the results reported in the two papers were not discussed by us, because the differences in the methods of precipitation used were sufficient to account for all, except Muer's preference for tablets of solid barium chloride instead of a barium chloride solution as a precipitant, and for only a limited amount of agitation after precipitation. As no definite results were given in support of these conclusions, we could not, of course, discuss them fully. The differences found only serve to emphasize the fact that the method used

in calibrating the turbidimeter must be carefully followed in all subsequent determinations. No originality is claimed for the turbidimetric method described in our paper; it is merely an account of the results obtained in an effort to adapt the method to a new use.

BUREAU OF STANDARDS
WASHINGTON, D. C.

R. S. MCBRIDE
E. R. WEAVER

THE CHEMICAL CONSTITUTION OF RESINOUS PHENOLIC CONDENSATION PRODUCTS—A CORRECTION

In my article under the above title, *THIS JOURNAL*, 5, 506, there is an error in the last line, page 511: "hexamethylenetetramine" should read "hexamethylenetetramintriphenol."

L. H. BAEKELAND.

BOOK REVIEWS

A Dictionary of Applied Chemistry. Second edition, revised and enlarged. By SIR EDWARD THORPE and other eminent contributors. To be issued in five volumes. Volume III, 789 pages. Price of complete set when issued, \$67.50. Price per volume, \$13.50. Longmans, Green and Company: London and New York.

This book is the third of the five volumes of the set. Volumes I and II were reviewed in *THIS JOURNAL*, 4, 550 and 698. Volume III closes with the chapter on Oils and Fats, following the usual alphabetical sequence. The same careful selection of eminent authors obtains in this as in the previous volumes, and a number of new names appear among the contributors. A comparison of the subject matter with that of the older edition shows careful revision and extension of the more important topics. A large amount of new matter has been added, for example, new chapters on Grape, Grape-seed Oil, Greases, Guaiacol, Guanidion, Gypsum, Halogen Acetic Acid, Helium, Hordenine, Hydantoin, Hydrolysis, Indigo (natural and artificial), Invertase, Iridium, Isoprene, Lacquer, Lactic Acid, Lactones, Lard, Leucine, Liquefaction of Gases, Liquors and Cordials, Meat Extracts, Mercerizing, Metallography, Monazite, Monel Metal, Neodymium, Utilization of Atmospheric Nitrogen.

The book is excellently printed on a paper well adapted to reference use. The binding is strong and substantial as in previous volumes.

It is hoped that the additional two volumes to complete the set will appear promptly. In this revised form the set will be a welcome addition to the working equipment of every works office, laboratory and reference library.

M. C. WHITAKER

Methods for the Analyses of Iron and Steel, Used in Laboratories of the American Rolling Mill Co., Middletown, Ohio. pp. 62. Illustrations 7. The Republican Publishing Co., Hamilton, Ohio.

The preface states that this bulletin is issued on account of the numerous requests received for copies of the methods used in the laboratories of the American Rolling Mill Co., especially those referring to the analysis of American Ingot Iron. The methods given for the ordinary elements are those of common use in iron and steel laboratories, and no claim is made for originality. The bulletin is intended as an aid to experienced chemists, thoroughly conversant with the standard methods for the analysis of iron and steel. For detail of method the reader is referred to standard text books with the exception of the determinations of nitrogen, hydrogen, and oxygen in steel, which are given in detail. Criticism and suggestions are invited in reference to new or modifications of old methods.

WILLIAM BRADY

Coal, Its Composition, Analysis, Utilization and Valuation. E. E. SOMERMEIER. 167 pages. Illustrations and tables. New York: McGraw-Hill Book Co. 1912. Price, \$2.00.

This book contains a very complete and readable presentation of coal testing, including sampling, analysis, calorific determinations, flue gas analysis, boiler test calculations, coal washing tests, etc. It is written with a view to meeting the demand of

the mechanical engineer, chemist, as well as the practical business man whether a seller or purchaser of coal, on all subjects relating to same. Tables of analyses of coals from all parts of the United States are included.

The book is particularly valuable to the chemist as it goes into details relating to methods of coal and flue gas analysis and calorimetric determinations, giving ample details of procedure, and points out many possible causes of errors, their relative importance, and means of obviating or correcting for same. Much of this data is original and is so important that every chemist who has to do with coal analysis should consult this work.

The book appears to be a little weak on a few points where the author has expressed opinions or made statements that are not in accordance with the most recent research work on the subjects without presenting any data or proof to substantiate same. This is especially so in connection with "Sampling Coal and Fusibility of Ash." Also in connection with calorimetric work and thermometer calibration, the author rather minimizes the work of the U. S. Bureau of Standards, while the advantage and need of referring all standardization work to them should have been emphasized.

E. G. BAILEY

Electroplating. A treatise on the Electro-deposition of Metals with a chapter on metal coloring and bronzing. By WILLIAM R. BARCLAY AND CECIL H. HAINSWORTH. Longmans, Green & Co. pp. 399. Price, \$2.10, net.

This volume is probably the most up-to-date book in English that we have on this subject. The first 116 pages are devoted to accessory knowledge in chemistry and electricity, which every electroplater should know, but of which few have any understanding. Thus we have short chapters on fundamental principles of chemistry, electrochemistry, electricity, primary batteries, the lead storage battery, the dynamo, etc. While this information is available in many other sources it is probably an advantage to have it included in a book on electroplating, thus bringing it directly to the attention of the electroplater.

In the discussion of voltage calculation on pages 67 and 68 according to the Kelvin equation, the shortcomings of the method are not mentioned, which is unfortunate.

Chapters VII and VIII describe the details of the plant for electroplating, construction of vats, rheostats, electrical measuring instruments, cleaning, scouring, sand blast, etc. All of this is well treated and considered in a practical manner. The rest of the book deals with the electro-deposition of silver, copper, nickel, gold, zinc, brass, iron, cobalt, tin, platinum, etc., in a very thorough way. The control of the baths is described and analytical methods given. The formulas for the different baths appear to have been carefully chosen. References are given in many cases, and some of these refer to recent work in this line. For example, Field's admirable work on brass is referred to, and also Kern's copper, nickel, and zinc baths.

The last chapters are devoted to metal coloring and finishing. Taken as a whole the book is excellent and should prove extremely useful.

S. A. TUCKER

Food Inspection and Analysis. For the use of public analysts, health officers, sanitary chemists and food economists. By ALBERT E. LEACH, S.B., late Chief of the Denver Food and Drug Inspection Laboratory, Bureau of Chemistry, U. S. Department of Agriculture. Third Edition. Revised and enlarged by ANDREW L. WINTON, Ph.D., Chief of Chicago Food and Drug Inspection Laboratory, Bureau of Chemistry, U. S. Department of Agriculture. New York: John Wiley & Sons. Large 8vo. xxi + 1001 pp., 120 figures, 40 full page half-tone plates. Cloth. Price, \$7.50 net.

This very popular treatise is so well known that a detailed description of it is unnecessary. "The period since the appearance of the second edition has been, in America, one of steady progress in food science as compared with the period of special activity, stimulated by federal legislation, immediately preceding and the pioneer period, in which the author was a prominent figure, that led to the publication of the first edition. Without changing the general plan of the work, which ought ever to remain as a monument to the author's remarkable grasp of the subject, new matter equivalent to about 80 pages, not including some 40 pages changed in the last thousand of the second edition, and 12 new cuts, have been added. The size of the work, however, has been increased but 47 pages, as much antiquated matter has been replaced by new, thus performing a double service to the reader."

The text of the book is divided into twenty-one chapters as follows:

Chapter I, pp. 1-13, discusses Food Analysis and Official Control.

Chapter II, pp. 14-38, The Laboratory and Its Equipment. A cut showing the Freas electric drying and constant temperature oven is a new addition to the discussion of laboratory equipment.

Chapter III, pp. 39-52. While this chapter is called Food, Its Functions, Proximate Components, and Nutritive Value, the major part consists of the classification and discussion of the proteins. The small part devoted to nutritive value of foods is very inadequate; it is rather strange that the old Rubner physiological fuel values have not been replaced by the more correct figures of Atwater which are so generally used at the present time.

Chapter IV, pp. 53-80, General Analytical Methods. The reviser has improved this chapter by giving a more complete discussion of the modern methods for the detection and determination of arsenic than was to be found in the old edition. Apparatus for drying in an atmosphere of hydrogen and the Hoskins electric furnace for ashing are illustrated and described.

Chapter V, pp. 81-99, The Microscope in Food Analysis.

Chapter VI, pp. 100-103, The Refractometer. These chapters remain unchanged.

Chapter VII, pp. 124-210, is on Milk and Milk Products. This chapter shows careful revision—cuts illustrating new forms of Babcock apparatus are substituted for the old ones and the discussions of the methods, *e. g.*, in the case of the detection of nitrates, have been augmented in order to include improvements which have appeared since the publication of the second edition. The sub-chapters on condensed milk, cream, and ice-cream have been very much improved, a process for the detection of foreign fat constituting a new and valuable addition.

Chapter VIII, pp. 211-269, is headed Flesh Foods. The sub-chapter on meats contains the discussion of the composition, wholesomeness and effect of treatment as in the earlier edition; the number of analytical methods, however, has been increased by methods for the determination of ammonia in meat and of acidity of fat. A paragraph on the effects of floating of shell-fish is new to this chapter.

Chapter IX, pp. 261-270, Eggs.

Chapter X, pp. 271-364, Cereals and Their Products, Legumes, Vegetables and Fruits. This chapter has been rewritten and

improved in several places, especially the part devoted to flour. A method for the determination of sugar in cereal products is a noteworthy addition; the sub-chapters on yeast and baking powders contain some new material.

Chapter XI, pp. 365-407, Tea, Coffee and Cocoa. The sub-chapter on tea contains the new methods for detection of "facing." The determination of sucrose and lactose in cocoa products assumes a new form.

Chapter XII, pp. 408-470, Spices. Several parts of this chapter have been rewritten.

Chapter XIII, pp. 471-564, Edible Fats and Oils. No important change.

Chapter XIV, pp. 565-652, Sugar and Saccharine Products. The description of several of the analytical methods in this chapter have been revised and brought up-to-date; Munson and Walker's lactose table has been corrected and more accurate tables of the relation between density and percentage of sugar solutions supplant the old one on pages 617 to 620.

Chapter XV, pp. 653-758, headed Alcoholic Beverages, has undergone a couple of slight changes. The Bureau of Standards table for the calculation of the percentage of alcohol-water solutions from the densities is not to be found.

Chapter XVI, pp. 759-781, on Vinegar has been enlarged in order to contain a method for the determination of glycerol in vinegar.

Chapters XVII, pp. 782-820, Artificial Food Colors. In addition to the extensive schemes for the separation and identification of the various dyestuffs used in sophistication of food material contained in the old edition, there are presented Price's scheme for separating the seven permitted colors and Mathewson's method for the quantitative separation of acid coal tar colors.

Chapter XVIII, pp. 821-849, Food Preservatives. A sub-chapter on a new food preservative, formic acid, has been added.

Chapter XIX, pp. 850-856, Artificial Sweeteners.

Chapter XX, pp. 857-899, Flavoring Extracts and Their Substitutes. The section devoted to vanilla extract has been revised to include several new methods, tests and a "summary of the analyses of authentic samples of vanilla extract." The lemon extract sub-chapter contains a new section devoted to the methods of analysis of lemon oil (also applicable to orange oil). Ginger extract is given place in this chapter.

Chapter XXI, pp. 900-964, on Vegetable and Fruit Products, has been completely revised and widened in scope to embody, according to the revising author's preface, "new sections on tomato ketchup, dried fruits, preserves (including maraschino cherries), fruit juices, and non-alcoholic carbonated beverages." "In the final chapter are included descriptions of recent methods for the determination of tin, vegetable acids, and habit-forming drugs, and for the detection of saponin, also microscopic methods for the detection of spoilage."

Following the final chapter there is an appendix containing the amended Federal Pure Food Law and the Meat Inspection Law. The 40 excellent photomicrographic plates are conveniently placed at the back of the book as in the past editions.

The reference lists following the chapters do not seem to have been so carefully revised as the general text of the book. While the recent work published in the government bulletins has been included in these reference lists, it is to be regretted that much that has appeared in the general chemical literature since the publication of the second edition of Leach's book has been omitted. Dr. Winton's revision, however, has greatly strengthened and improved the text of the treatise making it a valuable addition to the libraries of "public analysts, health officers, sanitary chemists and food economists."

A. W. THOMAS

NEW PUBLICATIONS

By D. D. HEROLDHEIMER, Librarian, Chemists' Club, New York

Alloys and their Technical Utilization. By A. LEIDERER. 4th edition. 8vo. 211 pp. Price, \$1.00. M. KRAVAT, Berlin. (German.)

Asphalt Construction for Pavements and Highways. By CLIFFORD RICHARDSON. 8th. 8vo. 188 pp. Price, \$2.00.

Boilers, Modern Steam. By W. D. WASSERBROUGH. 8vo. 168 pp. Price, \$1.25. C. Lockwood, London.

Chemistry, General Crystallography and Mineralogy. By E. VON MEYER and FR. RINNE. 10th. 8vo. 650 pp. Price, \$5.50. B. G. Teubner, Leipzig.

Colloidal State of Matter, The. (Translation.) By LEONARDO CASSUTO. 8vo. 247 pp. Price, \$2.00. Theodor Steinkopff, Dresden. (German.)

Colors, Oils and Varnishes, A Manual of Painters'. By GEORGE H. HURST and NOEL HEATON. 5th edition. 8vo. 528 pp. Price, \$2.75. Charles Griffin & Co., London.

Dictionary of Applied Chemistry, IV: Oilstone Soda-Nitre. By EDWARD THORPE. Vol. 5. Revised edition. 8vo. Price, \$12.00. Longmans, Green & Co., New York.

Dyeing, Chemical Products for Use in. By P. HEERMANN. 2nd edition. 8vo. 444 pp. U. Hoepli, Milan. (Italian.)

Electrochemical Practice. By ERICH MUELLER. 8vo. 221 pp. Price, \$2.00. Th. Steinkopff, Dresden. (German.)

Electrochemistry, Yearbook of, and Applied Physical Chemistry, XIII, 1906. By H. DANNEFELD and JULIUS MEYER. 8vo. 823 pp. Price, \$8.00. Wilhelm Knapp, Halle. (German.)

Engine, The Gas, Petrol and Oil. By D. CLERK and G. A. BURLS. Vol. 2. 8vo. 838 pp. Price, \$7.50. John Wiley & Sons, New York.

Finishing, Manual of Cloth. By EDITORS, *Dyer and Calico Printer*. 8vo. 300 pp. Price, \$6.50. Heywood & Co., London.

Gas Analysis. By L. M. DENNIS. 12mo. 434 pp. Price, \$2.10. The Macmillan Co., New York.

Gas Analysis Laboratories, Apparatus for, at Coal Mines. By GEO. A. BURRELL and FRANK M. SEIBERT. 8vo. 24 pp. U. S. Bureau of Mines, Technical Paper 14.

Gas Companies, Directory of American. By E. C. BROWN. L. 8vo. 768 pp. Price, \$5.00. The Gas Age, New York.

Gas Engineers and Managers, Handbook for. By NEWBIGGINGS. 8th edition. 8vo. Price, \$4.50. Walter King, London.

Gas Mantles, Illumination by Means of. By C. RICHARD BOEHM. 8vo. 62 pp. Gustav Heydenreich, Charlottenburg.

Gas Power. By C. F. HIRSCHFELD and T. C. ULBRECHT. 8vo. Price, \$1.50. Chapman & Hall, London.

Illuminating Gas, Quality Standard for. By JOINT COMMITTEE ON CALORIMETRY. 4°. 94 pp. Empire State Gas & Electric Association, New York.

Inorganic Chemistry for Engineers. By F. DUPRÉ. 8vo. 173 pp. Oskar Leiner, Leipzig. (German.)

Inorganic Chemistry, Textbook of. By A. F. HOLLEMAN. 11th edition. 8vo. 463 pp. Price, \$2.50. Veit & Co., Leipzig.

Inorganic Chemistry, Handbook of the Working Methods of. Vol. 1. By A. STAEBLER. Vol. 2. 8vo. 742 pp. Price, \$7.00. Veit & Co., Leipzig. (German.)

Iron, The Metallurgy of. By PAUL DOMNER, et al. 8vo. Price, \$2.00. Vinbert, Paris. (French.)

Iron, Using the Etching Process for the Testing of, by Means of the Microscope. By E. PREUSS. 8vo. Price, \$1.50. Julius Springer, Berlin. (German.)

Liquid Air, Production, Use and Storing. By OSCAR KAUSCH. 4th edition. L. 8vo. 463 pp. Price, \$2.50. Carl Steinart, Weimar. (German.)

Metal Casting. By E. A. SCHOTT. 8vo. Price, \$3.50. Bernh. Friedr. Voigt, Leipzig.

Metallic Alloys, Their Structure and Constitution. By G. H. GULLIVER. 2nd edition. Cr. 8vo. 438 pp. Price, \$2.75. C. Griffin & Co., London.

Metallurgy, Introduction to the Study of. By HENRY LE CHATELIER. 8vo. Price, \$2.25. Dunod & Pinat, Paris. (French.)

Metallurgy and Assaying, Textbook of Experimental. By A. R. GOWER. Cr. 8vo. 178 pp. Price, \$1.00. Chapman & Hall, London.

Natural Gas, Wastes in the Production and Utilization of, and Means for their Prevention. By RALPH ARNOLD and FREDERICK G. CLAPP. 8vo. 29 pp. U. S. Bureau of Mines, Technical Paper 38.

Petroleum: Production, Industry and Commerce. By L. WENGER. 8vo. Price, \$1.25. A. Rousseau, Paris. (French.)

Petroleum, A Treatise on. By BOVERTON REDWOOD. Vol. 3. 3rd edition. 8vo. 1000 pp. Price, \$12.50. C. Griffin & Co., London.

Producer-Gas Power Plant, The Commercial Trend of the, in the United States. By R. H. FERNALD. 8vo. 93 pp. U. S. Bureau of Mines, Bulletin 55.

Radium New Journal. 8vo. Monthly. About 14 pp. Began with April, 1913, number. The Radium Publishing Co., Pittsburgh. Forbes & Meyer, N.Y.C.

Rubber Tree. By W. F. DE BOIS MACLAREN. 8vo. 300 pp. Price, \$3.00. MacLaren & Sons, London.

Service Chemistry. By VIVIAN B. LEWIS. 4th edition. Cr. 8vo. 576 pp. Price, \$4.20. Longmans, Green & Co., New York.

Sewage: Trade Waste Waters and their Nature and Disposal. By J. MACLEAN WILSON and H. T. CALVERT. 8vo. 331 pp. Price, \$5.00. J. B. Lippincott Co., New York.

Steel, Standard Specifications for. By COMMITTEE ON STANDARD SPECIFICATIONS. 8vo. Price, \$1.50. American Society for Testing Materials, Philadelphia.

Textiles, The Vegetable. By J. BEAUVERIE. 8vo. 290 pp. Price, \$4.50. Gauthier Villars, Paris. (French.)

Tin Working, The Technic of. By F. GEORGI and A. SCHUBERT. 8vo. 160 pp. Price, \$1.25. M. Jaenecke, Leipzig. (German.)

Waters and Water Supplies, The Examination of. By JOHN C. THRESH. 2nd edition. 8vo. 644 pp. Price, \$4.50. J. & A. Churchill, London.

Water Supplies, The Purification of Public. By GEORGE A. JOHNSON. 8vo. 84 pp. U. S. Geological Survey, Water Supply Paper 315.

Zinc and Cadmium and their Production from Ores and By-products. By R. G. MAX LIEBIG. 8vo. Price, \$7.50. Otto Spamer, Leipzig.

RECENT JOURNAL ARTICLES

Alcohol, Quantitative Determination of Methyl and Ethyl, in Mixtures of Both. By JULIUS MEYERFELD. *Chemiker Zeitung*, Vol. 37, 1913, No. 64, pp. 649-651.

Alkaloid Silicotungstates. By HAROLD R. JENSEN. *Pharmaceutical Journal*, Vol. 90, 1913, No. 2586, pp. 658-660.

Barite, The Technical Manufacture of. By L. MARINO and D. DANESI. *Gazzetta Chimica Italiana*, Vol. 43, I, 1913, No. 5, pp. 416-439.

Catalysis by Oxidation and Reduction. By H. HEINRICH FRANCK. *Zeitschrift fuer angewandte Chemie*, 26 Aufsatzteil, 1913, No. 43, pp. 313-316.

Copper, The Sulfid Ores of. By L. C. GRATON and JOSEPH MURDOCH. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 77, pp. 741-811.

Dyes, Vat, Their Uses, Properties and Methods of Applications. ANONYMOUS. *Textile Colorist*, Vol. 35, 1913, No. 413, pp. 113-138.

Efficiency Bibliography. By N. H. B. MEYER, Bibliographer of the Library of Congress. May issue of *Special Libraries*. Nearly 1200 titles. Price, \$0.25. Special Libraries Association, 93 Broad St., Boston.

Ethyl Alcohol, New Method of Determining. By GEO. B. FRANKFORTER and FRANCIS C. FRARY. *Journal of Physical Chemistry*, Vol. 17, 1913, No. 5, pp. 402-473.

Fermentation Industry in 1912, Progress in the Chemistry of the. By O. MOHR. *Zeitschrift fuer angewandte Chemie*, 26 Aufsatzteil, 1913, No. 43, pp. 305-313.

Fibers and Textiles in 1912. By WILHELM MASSOT. *Zeitschrift fuer angewandte Chemie*, 26 Aufsatzteil, 1913, No. 37, pp. 257-271.

Furnaces, Some Fundamental Faults of Present-Day, and their Remedies. By ALLEYNE REYNOLDS. *Engineering*, Vol. 95, 1913, No. 2471, pp. 646-651.

Gas Engines and their Applications. By WILLIAM H. EDMONDSON. *The Gas Age*, Vol. 31, 1913, No. 11, pp. 551-555.

Gas, Some Notes on Carbonization. By ERNEST A. FRANKS. *Journal of Gas Lighting*, Vol. 122, 1913, No. 2612, pp. 667-669.

Heating Apparatus, Electric, for Laboratories. By CHARLES FRIBOURG. *International Sugar Journal*, Vol. 15, 1913, No. 173, pp. 219-222.

Lipochromes, or Fat-Soluble Coloring Matters of Natural Origin, Recent Advances in the Chemistry of. By G. W. MONIER-WILLIAMS. *Chemical World*, Vol. 2, 1913, No. 6, pp. 179-181.

Nitrogen, The Fixation of, by Mixtures of Barium Oxid and Charcoal. By THOMAS EWAN. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 9, pp. 467-474.

Oil Analysis, Methods of. By CHARLES EACHUS. *Journal of the American Leather Chemists' Association*, Vol. 8, 1913, No. 6, pp. 237-243.

Paints, Leadless, Lead and Zinc Pigments Compared. By R. CLAUDE BUSSELL. *Paint, Oil & Drug Review*, Vol. 55, 1913, No. 23, pp. 10-13.

Precipitation, Electrical, of Suspended Particles. By LINN BRADLEY. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 3, pp. 111-134.

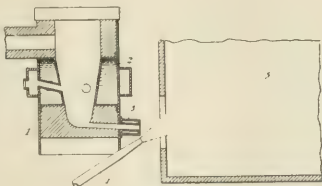
Rubber Solutions, Determination of the Degree of Viscosity of. By P. SCHIDROWITZ and H. A. GOLDSBROUGH. *India Rubber Journal*, Vol. 45, 1913, No. 17, pp. 16-17.

RECENT INVENTIONS

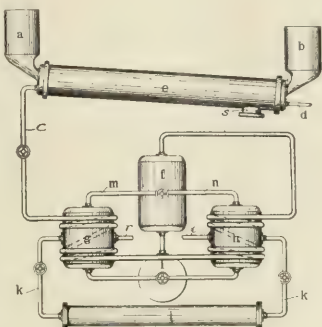
By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Portland Cement. T. A. Edison, April 22, 1913. U. S. Patent 1,059,661. This is a process intended for use in making Portland cement in localities where the conditions as to raw material are unfavorable for working by the usual methods.

The cement-making material with coal or coke in the proper amount to effect the fusion are introduced into the water-jacketed furnace 1. Quartz may be employed as the source of silica and clay as the source of alumina. A small percentage of oxid of iron is employed as well as limestone to permit fusion at a low temperature. The temperature necessary for fusion is from 1800° to a little below 2500° F. and there is produced an extremely liquid, non-viscid slag containing approximately 50% of lime. This is subjected to a powerful blast which chills and finely subdivides it. To this, sufficient limestone is added to give the proportion of lime desired for the cement and the mixture is then calcined.

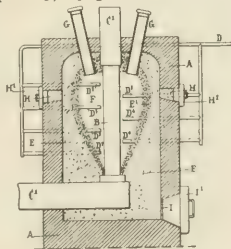


Potash and Cement Clinker. S. Gelléri, April 8, 1913. U. S. Patent 1,058,686. Silicates containing alkali metal compounds are burned with a salt of an alkaline earth metal. The residue is subjected to the action of ammonium carbonate vapors under high pressure in a closed chamber to render the alkali soluble. The alkalies are then leached out and the residue again burned.



Persulfates. G. Adolph and A. Pietzsch, April 22, 1913. U. S. Patent 1,059,809. A bath containing ammonium sulfate and undissolved potassium sulfate is subjected to electrolysis, fresh supplies of solid potassium sulfate being added from time to time to reconvert the persulfate of ammonium produced into the sulfate.

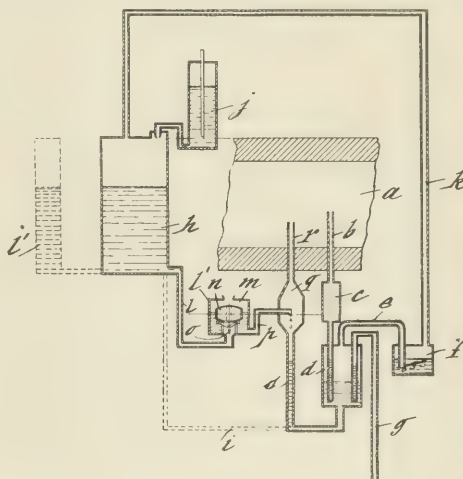
Aluminium Nitrid. O. Serpek, April 29, 1913. U. S. Patent 1,060,509. In this process aluminium nitrid is produced by heating alumina and carbon in a current of nitrogen in a stationary furnace. The heating is effected by means of electrical resistance, the nitrogen being supplied in the immediate neighborhood of the resistance and forming a cavity between the resistance and the nitrid produced.



Catalyzer for Hydrogenating Oils and the Like. C. Ellis, May 6, 1913. U. S. Pat. 1,060,673. The material consists of finely granular active charcoal coated but not substantially impregnated with reduced nickel.

Automatic Gas-Analyzer. A. Mertens, May 6, 1913. U. S. Pat. 1,060,996. This apparatus is particularly designed for measuring the percentage of carbonic acid in the products of combustion of a furnace. In the illustration, *a* indicates the smoke flue which is connected by a pipe, *b*, having a dust filter, *c*, with a gas measuring chamber, *d*, which is in turn connected with a gas-absorbing chamber, *f*, by pipe *e*.

The suction of the gas into the measuring vessel *d* is effected by the automatic emptying of the gas-measuring vessel through the medium of the siphon *g*. The forcing of the gas into the absorber *f* is effected through the feeding of the vessel *d* with water conducted from a receptacle, *h*, through pipe *i*. This operation is entirely automatic, the liquid flowing from the receptacle *h* into the vessel *d* until the moment when the siphon *g* automatically fills and causes the rapid emptying of the vessel *d*, which emptying is accompanied by a suction of gas which



stops when the siphon empties itself and the forcing of the gas sucked in recommences by a fresh arrival of liquid from the receptacle *h*.

The receptacle *h* is a closed vessel connected to a Mariotte bottle, *j*, regulated so as to cause the flow of a certain quantity of liquid from the receptacle *h* directly a depression is produced therein. Moreover, the absorber *f* is connected by a pipe, *k*, to the receptacle *h* so that the non-absorbed gas is forced into the receptacle *h*. The Mariotte bottle *j*, as well as the receptacle *h*, is provided with a graduation allowing of easily ascertaining the volumes of liquid which have flowed therefrom. Consequently when, at the end of a given time, it is desired to learn the mean proportion of carbonic acid contained in the products of combustion it is only necessary to take note of the quantity of liquid which has run from the Mariotte bottle *j* as well as the quantity of liquid which has run from the receptacle *h*. This latter quantity is easily determined by adding to the volume *V* indicated by the graduation as having flowed from the receptacle *h*, the volume *v* of the liquid which has flowed from the Mariotte bottle *j*. The ratio $v/(V + v)$ then immediately gives the proportion of the gas absorbed with relation to the total quantity of gas treated.

The apparatus is also provided with means which may be used if desired, to cause the volume of gas analyzed in any period of time to vary with the draft of the flue.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JUNE, 1913

ORGANIC CHEMICALS

Acetamid.....	Lb.	21	@	23
Acetic Acid (28 per cent).....	C.	2.00	@	2.15
Acetone (drums).....	Lb.	15 1/4	@	16
Alcohol, denatured (180 proof).....	Gal.	37	@	39
Alcohol, grain (188 proof).....	Gal.	2.46	@	2.48
Alcohol, wood (95 per cent).....	Gal.	49	@	52
Amyl Acetate.....	C.	2.35	@	2.55
Aniline Oil.....	Lb.	10 1/8	@	10 5/8
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	21	@	23
Camphor (refined in bulk).....	Lb.	42 1/2	@	44
Carbolic Acid (drums).....	Lb.	12	@	14 1/2
Carbon Bisulfide.....	Lb.	6 1/2	@	8
Carbon Tetrachloride (drums).....	Lb.	8	@	8 1/2
Chloroform.....	Lb.	25	@	35
Citric Acid (domestic), crystals.....	Lb.	41 1/2	@	42 1/2
Dextrine (corn).....	C.	2.80	@	3.40
Dextrine (imported potato).....	Lb.	6	@	7
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	19	@	19 1/2
Oxalic Acid.....	Lb.	7 7/8	@	8
Pyrogallol Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	29	@	31
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2.02	/	2.50
Starch (potato).....	Lb.	4 1/4	@	5
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	23 1/8	@	23 1/4
Starch (wheat).....	Lb.	5	@	6 1/2
Tannic Acid (commercial).....	Lb.	35	@	35
Tartaric Acid, crystals.....	Lb.	30 1/4	@	31

INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 3/4	@	8
Acetate of Lime (gray).....	C.	2.50	@	2.60
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate.....	C.	1.40	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/8
Ammonium Chloride, gray.....	Lb.	6 1/4	@	6 1/2
Aqua Ammonia (drums) 16°.....	Lb.	21 1/4	@	21 1/2
Arsenic, white.....	Lb.	3 3/8	@	4
Barium Chloride.....	C.	1.70	@	1.80
Barium Nitrate.....	Lb.	5 1/4	@	5 1/2
Barytes (prime white, foreign).....	Ton	18.50	@	22.50
Bleaching Powder (35 per cent).....	C.	1.25	@	1.40
Blue Vitriol.....	Lb.	5 1/4	@	5 1/2
Borax, crystals (bags).....	Lb.	3 3/4	@	4 1/4
Boric Acid, crystals (powd.).....	Lb.	7	@	7 1/2
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	85	@	1.10
Chalk (light precipitated).....	Lb.	4	@	5
China Clay (imported).....	Ton	11.50	@	18.00
Feldspar.....	Ton	7.00	@	9.00
Fuller's Earth, powdered, Foreign.....	Ton	14.50	@	15.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.05	@	3.10
Lead Nitrate.....	Lb.	8 1/8	@	8 1/4
Litharge (American).....	Lb.	6 1/2	@	7
Lithium Carbonate.....	Lb.	65	@	70
Magnesia (powdered).....	Lb.	5 1/2	@	6
Magnesite (raw).....	Ton	30.00	@	31.00
Nitric Acid, 36°.....	Lb.	37 1/8	@	41 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	21 1/2	@	25 1/2
Phosphorus.....	Lb.	35	@	90
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 3/4	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined) 80 @ 85%.....	C.	3.40	@	3.65
Potassium Chlorate, crystals.....	Lb.	8 1/4	@	9 3/4
Potassium Cyanide (bulk) 98-99%.....	Lb.	19	@	24
Potassium Hydroxide.....	C.	3.75	@	4.75
Potassium Iodide (bulk).....	Lb.	2.60	@	2.65
Potassium Nitrate (crude).....	Lb.	5	@	—
Potassium Permanganate (bulk).....	Lb.	93 1/4	@	11
Quicksilver, Flask.....	40.00	@	—	—
Red Lead (American).....	Lb.	6 1/2	@	7
Salt Cake (glass-makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	37 3/4	@	39
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	65	@	70
Sodium Acetate.....	Lb.	4	@	4 1/2
Sodium Bicarbonate (domestic).....	Lb.	1	@	1 1/8
Sodium Bicarbonate (English).....	Lb.	29 1/4	@	3
Sodium Bichromate.....	Lb.	4 1/2	@	4 7/8
Sodium Carbonate (dry).....	Lb.	60	@	80
Sodium Chlorate.....	Lb.	8 1/4	@	9 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.57 1/2	@	1.62 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	2.40	@	2.45
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	67 1/8	@	75 1/8
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	14 1/4	@	14 1/2
Tin Oxide.....	Lb.	48	@	50
White Lead (American, dry).....	Lb.	5 1/4	@	6
Zinc Carbonate.....	Lb.	10 1/2	@	11 1/2
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 3/8	@	6 3/8
Zinc Sulfate.....	Lb.	21 1/2	@	23 1/4

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	42	@	45
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	87 1/8	@	10
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	5.70	@	6.00
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	47	@	—
Cottonseed Oil (p. s. y.).....	Lb.	7 5/8	@	7 7/8
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	9 1/8	@	9 3/4
Lard Oil (prime winter).....	Gal.	94	@	98
Linseed Oil (double-boiled).....	Gal.	48	@	49
Menhaden Oil (crude).....	Gal.	27	@	28
Neatsfoot Oil (20°).....	Gal.	98	@	1.10
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2	@	3 3/4
Paraffine Oil (high viscosity).....	Gal.	26	@	28
Rosin ("F" grade).....	Bbl.	4.80	@	5.00
Rosin Oil (first run).....	Gal.	30	@	34
Shellac, T. N.....	Lb.	21	@	22
Spermaceti (cake).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9 1/8	@	10
Tallow (acidless).....	Gal.	64	@	67
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	39 1/2	@	40

METALS

Aluminum (No. 1 ingots).....	Lb.	24 1/2	@	25
Antimony (Hallet's).....	Lb.	8 1/4	@	8 3/4
Bismuth (New York).....	Lb.	2.10	@	2.15
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	Lb.	14 3/4	@	15
Copper (lake).....	Lb.	147 1/8	@	151 1/8
Lead, N. Y.....	Lb.	4.32 1/2	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	46.00	@	—
Silver.....	Oz.	58 3/8	@	60
Tin.....	Lb.	45.10	@	46
Zinc.....	Lb.	5.10	@	5 1/8

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.95	@	3.00
Blood, dried.....	Unit	2.85	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	27.50	@	28.00
Calcium Nitrate (Norwegian).....	C.	2.40	@	—
Castor meal.....	Unit	nominal	@	—
Fish Scrap, domestic, dried.....	Unit	nominal	@	—
Mowrah meal.....	Ton	nominal	@	—
Phosphate, acid, 16 per cent bulk.....	Ton	7.00	@	7.50
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	3.00	@	3.25
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	38.55	@	—
Pyrites, furnace size, imported.....	Unit	0.13 1/2	@	—
Tankage, high-grade.....	Unit	2.75	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

AUGUST, 1913

No. 8

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblentz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City
Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City
Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.
No claims will be allowed unless made within 60 days

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:	What's the Matter with the American Chemist? By Daniel M. Grosh	692
United States Forestry Service Investigations	General Efficiency in Dye-Houses and Bleach Works. By Louis Joseph Mátyos	693
What's the Matter with the American Chemist?		626
ORIGINAL PAPERS:	CURRENT INDUSTRIAL NEWS:	
The Constitution of Portland Cement Clinker. By Edward D. Campbell	The Consumption of Oxygen	695
The Drying Rates of Raw Paint Oils—A Comparison. By L. V. Redman, A. J. Weith and F. P. Brock	Hardening Steel with Compressed Air	695
The Gases Formed in Anaerobic Sewage Decomposition. By R. H. Jesse, Jr.	The Production of Vanadium Steel	695
A Modified Form of Stability Test for Explosives. By H. C. P. Weber	A German Soot and Cinder Arrester	696
Kukui (Candle-Nut) Oil. By Alice R. Thompson	The Manufacture of Carbon Black from Natural Gas	696
The Determination of Sodium Borate in Soap. By Paul Poetschke	A Plant for the Treatment of Iron Pyrites	697
Determination of Phosphorus in Steels Containing Vanadium. By J. R. Cain and F. H. Tucker	The Deposition of Nickel	697
A Rapid Modified Chlorplatinate Method for the Estimation of Potassium. By W. B. Hicks	Tungsten Filament Lamps	697
The Chemical Composition of Cooked Vegetable Foods, Part III. By Katharine I. Williams	The Platinum Market	697
Peppermint Oil Industry in Japan. By Yeinosuke Shinosaki	The Manufacture of Salt	698
On Japanese Peppermint Oil. By Yeinosuke Shinosaki	Proposed Development of American Potash Deposits	698
The Use of the Immersion Refractometer in Examining American Beers Made from Malt and Unmalted Cereals. By Robert Schwarz	The Fertilizer Industry of Charleston, S. C.	698
Calcium Thioarsenate as a Spray. By S. H. Katz and P. D. Buckminster	The Consumption of Various Nitrogen-Fertilizers in Austria	698
The Condition of Soil Phosphoric Acid Insoluble in Hydrochloric Acid. By William H. Fry	The Gas Industry of England	699
Analyses of Confectioners' Glucose. By Edward Gudeman	The Purification of Coal Gas	699
Influence of Ozone on Yeast and Bacteria. By Carl A. Nowak	The Manufacture of Gas from Sewage Sludge	700
Determination of Small Amounts of Caffeine. A Comparison of Methods. By B. L. Murray	The Caucasian Petroleum Industry	701
LABORATORY AND PLANT:	The Condition of the Scottish Shale Oil Industry	701
The Distribution of Heat in the Operation of Steam Boilers. By Perry Barker	SCIENTIFIC SOCIETIES:	
Chemistry in Relation to the Frozen Meat Industry of New Zealand. By A. M. Wright	American Chemical Society—Rochester Meeting	701
The Determination of the Melting Point of Greases by Means of the New York Testing Laboratory Viscosimeter. By Hermann W. Mahr	New Section on Water, Sewerage and Sanitation at Rochester Meeting	702
Convenient Device for Analytical Ignitions. By Edward D. Campbell	The Annual Convention of the American Institute of Electrical Engineers	702
ADDRESSES:	International Association of Chemical Societies	703
Efficiency in Chemical Industries. By T. B. Wagner	NOTES AND CORRESPONDENCE:	
Utilizing Wood Waste. By John E. Teeple	German Manufacture of Barium Compounds	703
The Relation of the Manufacturer to Our Patent System. By W. M. Grosvenor	Peat as Fuel	704
	Life of Platinum Crucibles Lengthened by Substitution of Meker Burner for Blast Lamp in Carbon Determinations	705
	Synthetic Tannin	705
	Imports of Olive Oil Not Adulterated	706
	Crisis in German Potash Industry	706
	Power from Waste Heat	706
	German Record Production of Raw Iron	706
	BOOK REVIEWS:	
	A Manual of Cement Testing; Coal, and the Prevention of Explosions and Fires in Mines; "New and Non-official Remedies, 1911;" The Natural History of Clay	707
	NEW PUBLICATIONS	708
	RECENT INVENTIONS	709
	MARKET REPORT	710

EDITORIALS

UNITED STATES FORESTRY SERVICE INVESTIGATIONS

The first number of a new publication entitled *Review of Forestry Service Investigations* (Vol. I, pp. 1-68, pl. I-VIII, Mar. 11, 1912) has just been received. The purpose of this publication is to keep the entire force in touch with the work of the Forest Service—its scope, progress and accomplishments. By keeping the men informed as to the nature and development of the work in all its branches, it will enable them to coordinate more completely their investigations as well as to conduct them according to the most improved methods. The succeeding numbers will be issued as the material accumulated permits.

The present number is of unusual interest. It contains the first complete outline of the extent and nature of the work undertaken by our Forestry Service. It shows the nature of the present organization, established January, 1912, and the various lines of investigation that are being followed out at present. The work as now organized falls under four main divisions:

1. Dendrology, covering forest distribution and wood structure.

2. Grazing, or the relation and utilization of forage crops in and adjacent to forests without danger to the forests and watershed. The field of work here is a broad one, the investigations covering such subjects as artificial and natural seeding, the production of the maximum value of forage crops, methods of handling stock on the range, etc.

3. Products: The aim of this work is to obtain authentic information regarding properties and suitability for different purposes of various species and kinds of forest products. The investigations deal with wood preservation, pulping processes, distillation, etc.

4. Silviculture: The purpose of this division is to secure a thorough knowledge of the nature and requirements of all forest trees in order that existing forests may be handled in a scientific manner and that new forests may be established to secure the best returns in timber and other forest products. This broad field covers investigations in forestation; forest influence upon climate, stream flow, erosion; forest management, protection, utilization, etc.

The final twenty-four pages of the volume are devoted to an outline of the plan of work that has been approved for the ensuing year. Here we find all of the investigations that are now being carried out classified under the topics mentioned above. The nature and scope of the work is briefly stated and the sections of country in which the investigations will be carried out are given.

One can not look at this splendidly organized work without feeling a keen regret that the Forestry Service is so hampered by lack of funds and men. No country is so fortunately adapted, as regards climate, soil and species, for this work as America. Now for a long

time we have been conscious of the evils and dangers that are to come from a neglect of this resource of the nation and yet in the face of all of this there is the blighting influence of apathy and cheap politics. It is greatly to be desired that information of this nature, instead of reaching only the forest service and the few interested in this line of work, should be put out in a form so as to attract the attention of the voting mass of the people.

Past experiences would seem to warrant the belief that very little is to be expected from our politicians. They are like chips upon the water, bobbing any way a chance wind may blow them. They are like an administrative officer in charge of work concerning which he is ignorant. He can have no sympathy with the policies, owing to his ignorance of the nature and scope of the work. He can not advise or lead, because he does not understand, and naturally he is led this way and that way by every selfish interest that reaches him. The majority of our legislators are in the same situation. Neither by nature nor by training are they adapted to carry on the work in the positions to which they are elected. They can not exercise judgment concerning matters of which they are ignorant and their actions are very largely controlled by selfish interests and petty policies.

So imperative is the need of conducting the work of our forestry service upon a larger scale in accordance with the outlines of this bulletin that it would seem wise to devise some scheme of acquainting the people of the country with the nature of the problem that demands their immediate attention and action. It is not to be questioned that if the country were informed of the importance of this work, steps would be taken to give it adequate support.

C. C. CURTIS

WHAT'S THE MATTER WITH THE AMERICAN CHEMIST?

In the article on "What's the Matter with the American Chemist?" in this issue, Mr. Grosh seems to think that we have indeed entered upon parlous times, and that the lack of appreciation or coöperation between the manufacturer and the scientist is demoralizing the chemist. His principal illustration in support of his views is the American dyestuff industry; he laments the fact that our chemists cannot supply the home market with the required dyes so largely employed in the textile industry.

There is no gainsaying the fact that in spite of tariff protection and the high genius of American chemists in general, dyestuffs can be manufactured cheaper and better in Germany than in this country. The dyestuff industry in fact does not seem to be well adapted to the conditions obtaining here in America. In the first place, the manufacture of dyestuffs has heretofore necessitated large and specially trained corps of research chemists working more or less blindly in the hope of "getting something." In Germany there are numbers of chemists graduating from the universities

who are willing and content to enter the services of one of the several large color factories, accepting a small pittance for the privilege of working under conditions which may eventually lead to something worth while. The cost of living is comparatively small, and these young men are willing to accept mere living expenses in exchange for the opportunity to "make good."

The trouble with the American chemists in this connection is that they want to draw large salaries before they have really demonstrated to the manufacturer the ability to give ample value in return for the money he pays them. American manufacturers are perhaps as keen as those in any other country in making use of the chemist to develop their business, but they are very shy in buying a "pig in a poke." If the young chemist in this country would be satisfied to go into a manufacturing plant under conditions similar to those accepted by the young German chemist, there is no doubt but that large research laboratories could be organized; but, as a rule, the young man here in America can make a much better living under other conditions, and consequently he

pursues that line which demands the least sacrifice.

In the dyestuff industry another condition also prevails which makes it rather unattractive to the American manufacturer. Dyestuffs embrace a large number of compounds, and though the aggregate used in this country is large in quantity, nevertheless the amounts of the individual compounds themselves are not very great. Therefore the manufacturer would have to engage in the preparation of a large number of substances in comparatively small amounts, and this is not in accord with the best American practice, for the market would be limited almost entirely to the home country. If under American conditions, there were good profit to be made in the dyestuff industry, we feel sure this industry would have received its proper development in this country; but the American chemist, manufacturer, and capitalist have found more profitable outlets in other fields of endeavor, and have naturally followed the lines of least resistance. So the answer to the question "What's the Matter with the American Chemist?" is "Nothing."

J. M. MATTHEWS

ORIGINAL PAPERS

THE CONSTITUTION OF PORTLAND CEMENT CLINKER

By EDWARD D. CAMPBELL

Received June 26, 1913

With the attention now being given to the problem of determining the actual constituents of Portland cement, a description of an experimental method for the separation and analysis of alite and celite, formed at the ordinary clinkering temperature, may not be without interest.

Törnebohm and Le Chatelier, as early as 1897, described "alite" as the crystalline material separating out from an inter-crystalline magma, "celite." Törnebohm¹ further lays stress on the fact that celite is fusible at the clinkering temperature and promotes the crystallization of the alite. No claim is made that celite is a definite chemical or mineralogical entity, and it is according to this interpretation of the terms that they are used in this article.

In 1912, while attempting to study the equilibrium which would be established, at the clinkering temperature, in Portland cement clinker, E. G. Pierce, working in conjunction with the author, noticed that the pure magnesium oxide crucible, in which pieces of the clinker were being heated, was stained wherever these pieces were in contact with it and that this stain often spread over a considerable part of the crucible. This observation showed at once that some constituent of the clinker must be very fluid at the clinkering temperature so that under the proper conditions it might be separated from the main mass of the clinker by absorption in a manner exactly analogous to that employed when the mother liquor is withdrawn from crystals by means of a porous plate. This conception that, at the clinkering temperature, Portland cement

clinker consists of a mass of crystals bathed in the mother liquor from which they have crystallized and that this mother liquor may be drawn off from the crystals by means of a properly prepared porous plate, forms the basis for the work described in the present paper.

Considerable preliminary work was done by Mr. Pierce, but, owing to lack of time, the results obtained were not sufficiently conclusive to warrant publication. During the last year the work has been carried on by P. K. Fletcher and M. N. Taber, working under the direction of the author. Although there yet remains much to be done before the constitution of clinker will be thoroughly understood, the results given herein seem to be sufficiently significant to render their publication desirable.

The furnace used in the work was a Méker high temperature furnace described as No. 36 in the catalogue of the Scientific Materials Co., Pittsburgh, slightly modified as the needs of our work demanded. In this furnace the material under treatment is supported on a tripod and is surrounded by the flame from a Méker blast lamp situated below the bottom on which the tripod rests. The tripod used was made of aluminum cement and wrapped with platinum foil so that the material did not come in direct contact with it, the whole being surrounded by a cylinder of refractory ware through which the flame must ascend and around the outside of which the products of combustion must descend before being drawn off through the two chimneys located on opposite sides of the furnace near the bottom. This principle of construction enables a much higher temperature to be obtained than can usually be secured in small, gas-fired furnaces.

The temperatures were measured by means of a

¹ *Tonindustrie Z.*, **21**, 1148 (1897).

standard platinum-rhodium thermal couple, the head of which was protected by means of a short piece of Marquart tubing. The thermal couple was so placed that the head was in the annular space between the inner cylinder and the material under treatment and within ± 3 mm. of this latter. Temperature readings could be made with a reading error not exceeding two degrees and the temperature could be held constant for as long as desired with a variation of less than eight degrees. It is not thought that the temperatures recorded are more than 10° from their true value.

Some difficulty was encountered in determining the best method of preparing suitable absorbent plates. These were finally made in the form of discs about 30 mm. in diameter, 3-4 mm. in thickness, and weighing about 12 grams. These plates were placed with the clinker on one side and larger, heavier, magnesium oxide discs on the other, which, by their added capillary action insured the complete saturation of the small plates and the more complete removal of the celite from the clinker. These discs were prepared from Merck's C. P. magnesium oxide which was found on analysis to contain 0.01 per cent alumina, Al_2O_3 , and 0.03 per cent silica, SiO_2 , but was free from any trace of ferric oxide, Fe_2O_3 , or calcium oxide, CaO . Lots of 50 grams each of this magnesium oxide were packed in pure magnesium oxide crucibles and burned in the furnace at a temperature of 1500°C . for one hour. This preliminary burning shrinks the magnesium oxide to approximately one-half of its original volume. Four parts, by weight, of this burned magnesium oxide were then intimately mixed with one part of unburned magnesium oxide and to the whole was added strong magnesium chloride solution till a proper consistency was obtained to enable the mass to be moulded into discs with the aid of glass forms. The magnesium chloride solution used contained 250 grams of Kahlbaum's C. P. MgCl_2 to the liter. The discs, after removal from the forms, were thoroughly dried in a drying oven and became quite hard, owing to the formation of magnesium oxychloride cement which served as a binder. These discs were then stacked on the tripod, upon which had been first placed a thin disc of magnesium oxide covered by a disc of sheet platinum, thus insuring freedom from possible contamination, and burned at a temperature of 1500° for an hour and a quarter. This resulted in strong discs, the faces of which could be ground to a smooth finish thus insuring good contact with the faces of the discs of clinker which were similarly ground.

The material for making the clinkers in all experiments designated by the letter "A" was the raw mixture used by one of the largest Eastern cement mills. Several kilos of this material were ground for four hours in a porcelain lined jar mill to insure homogeneity and fineness. The material used in the experiments designated "B" was prepared by adding 8.42

per cent of Kahlbaum's C. P. calcium carbonate, CaCO_3 , to a weighed portion of the "A" mixture, thus maintaining constancy of the molecular ratios except that of the calcium oxide, CaO . The analysis of the "A" mixture was as follows:

SiO_2	14.33
Al_2O_3	4.44
Fe_2O_3	1.74
CaO	41.40
MgO	2.02
Undetermined.....	0.89
Loss on ignition.....	38.18

The discs of clinker made were prepared by taking the raw mixture, moistening with water and tamping firmly into cylindrical moulds 43 mm. in diameter and 22 mm. in height. After drying, these discs were burned in the same manner as the magnesium oxide discs. The temperature of burning of the "A" mixture was held at 1475°C . while that of the "B" mixture was 1550°C . In all cases the clinker was allowed to cool slowly with the furnace. The discs of clinker resulting from these burnings were about 30 mm. in diameter, 18 mm. thick and weighed from 32-35 grams each. Before using for an absorption the faces of the clinker were ground true.

In setting up an experiment to determine the percentage of celite absorbed in a given time and at a given temperature, two small and two large, hard burned, magnesium oxide discs were accurately ground and weighed. A disc of the clinker to be treated was similarly ground and weighed. These five were then stacked in the furnace as shown by Fig. 1 in the accompanying photograph. The temperature was then gradually raised until the thermal couple indicated the required temperature, at which

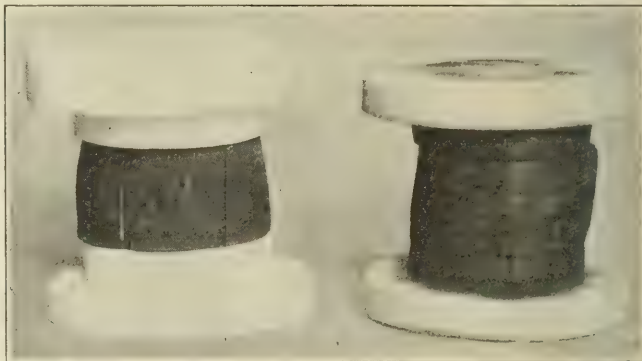


FIG. 1

FIG. 2

point it was held constant as long as desired. At the end of the burning the stack of material was allowed to cool slowly with the furnace. The appearance of a typical stack after the absorption is shown in Fig. 2. On removing a stack from the furnace the discs were usually found more or less firmly cemented together, but a complete separation of the magnesium oxide discs from the alite could be easily made. After this separation the discs were accurately weighed, the increase in weight of the magnesium oxide discs due

TABLE I

Experiment	Temperature ° C.	Time Hours	Per cent celite absorbed	Weight of constituents from 3-gram sample				Calculated wt. MgO	Total wt. in gms	Percentage composition of celite absorbed				
				SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
A ₁	1475	13	20.87	0.0432	0.0743	0.0320	0.2154	0.0205	0.3854	11.21	19.28	8.30	55.89	5.32
A ₂	1500	9	22.66	0.0433	0.0747	0.0323	0.2150	0.0205	0.3858	11.22	19.36	8.37	55.73	5.31
A ₃	1510	3	21.40	0.0476	0.0637	0.0279	0.1928	0.0173	0.3493	13.63	18.24	7.99	55.20	4.95
A ₄	1575	2 1/3	26.25	0.0476	0.0632	0.0277	0.1932	0.0173	0.3490	13.64	18.11	7.94	55.36	4.96
				0.0559	0.0671	0.0314	0.2161	0.0160	0.3865	14.46	17.36	8.12	55.91	4.15
B ₄	1575	8	20.80	0.0555	0.0669	0.0317	0.2157	0.0160	0.3858	14.39	17.34	8.22	55.91	4.15
				0.0353	0.0769	0.0343	0.2288	0.0113	0.3866	9.13	19.89	8.87	59.18	2.92
				0.0350	0.0766	0.0347	0.2282	0.0113	0.3858	9.07	19.86	8.99	59.15	2.93

to the absorbed celite being calculated to per cent of the original weight of the clinker.

In experiment A₃, Table II, three successive absorptions of three hours each were made, the magnesium oxide discs being changed in each case. The results of these absorptions show that of the celite withdrawn in the nine hours, 70 per cent was absorbed by the first set of discs, 25 per cent by the second, and only 5 per cent by the third.

TABLE II

Experiment	Temper- ature ° C.	Time Hours	Per cent celite absorbed	Percentage composition of impure alite and clinker				
				SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
CLINKERS								
A	1475	...	(clinker)	22.11	7.32	2.69	64.02	3.13
B	1500	...	(clinker)	20.61	6.82	2.51	66.46	2.91
ALITES								
A ₁	1475	13	20.87	25.89	2.58	1.04	67.78	2.52
A ₂	1500	3 + 3 + 3	22.66	25.83	2.56	1.04	67.81	2.56
				26.07	2.96	1.23	67.00	2.64
A ₃	1510	3	21.40	26.04	2.91	1.29	66.96	2.62
A ₄	1575	2 1/3	26.25	25.65	3.67	1.39	66.42	2.77
				25.71	3.66	1.29	66.47	2.71
B ₄	1575	8	20.80	23.34	1.76	0.74	71.14	2.91
				23.36	1.74	0.74	71.16	2.93

TABLE III—MOLECULAR RATIOS IN CELITE ABSORBED

Experiment	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	CaO	MgO
A ₁	100.0	27.6	98.4	526.5	69.7
A ₃	100.0	28.0	127.2	554.4	69.0
A ₄	100.0	30.1	140.9	587.4	60.6
B ₄	100.0	28.7	75.8	548.9	37.3

TABLE IV—MOLECULAR RATIOS IN IMPURE ALITE AND CLINKER

Experiment	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
CLINKERS					
A	100.0	19.5	4.6	311.4	21.1
B	100.0	19.5	4.6	346.6	21.1
ALITES					
A ₁	100.0	5.9	1.5	281.9	14.7
A ₂	100.0	6.6	1.8	276.5	15.1
A ₄	100.0	8.4	2.0	278.2	15.9
B ₄	100.0	4.4	1.2	327.7	18.7

The analyses of the clinker and of the alite were made by the methods usually employed for the accurate analysis of such materials. When attempts were made to analyze the magnesium oxide saturated with celite, accurate results could not be obtained on account of the interference from the high concentration of magnesium salts. In order to obtain large enough weights of SiO₂, Al₂O₃, Fe₂O₃, and CaO derived from celite to be satisfactory, three-gram samples of the small magnesium oxide discs were used in all cases. The finely ground material was easily and completely decomposed on digestion with hot dilute hydrochloric acid. The silica was removed by two evaporations. In order to obtain an accurate separation of the aluminium and ferric hydroxides from the magnesium

salts it was found necessary to make the first precipitation in the cold, allowing the precipitate to stand for three hours before filtering. By filtering and washing the precipitate thus obtained, redissolving and reprecipitating in the usual manner, a complete precipitation of the aluminium and ferric hydroxides free from magnesium compounds could be obtained. It was also found necessary to make the first precipitation of calcium oxalate in the cold by adding a moderate excess of ammonium oxalate to a solution rendered just alkaline with ammonia, a drop of methyl red being used as indicator. The first precipitate of calcium oxalate was allowed to settle about 20 hours, when it was washed two or three times by decantation, redissolved in a little hydrochloric acid and then reprecipitated in the usual manner.

The results of the analyses are shown in Tables I and II. Since tests show that all of the iron in both alite and celite exists in the ferric condition, when the burning is conducted in an oxidizing atmosphere, the iron is reported as Fe₂O₃. The per cent of magnesium oxide in the celite is calculated by assuming that the magnesium oxide of the clinker not accounted for by the analysis of the alite has been absorbed as a constituent of the celite.

The molecular ratios of the constituents in celite are given in Table III, while those of the clinker and of the impure alite are given in Table IV.

In order to determine whether celite possessed cementing qualities and whether the alite showed the presence of free calcium oxide, pats were made which, after remaining in a damp atmosphere for twenty-four hours, were subjected to the action of steam for six hours. The behavior of the pats under this test is shown in Table V.

TABLE V

MATERIAL OF PAT	CONDITION AFTER 6 HRS. IN STEAM
Pure MgO burned at 1500°.....	Expanded—loose from glass—moderately strong—slight cracks.
7 pts. 1500° MgO + 1 pt. cement.	Completely disintegrated and washed away.
MgO disc containing A ₁ celite.....	Soft, like mud.
MgO disc containing B ₄ celite.....	Soft, like mud.
A ₁ alite.....	Perfect—strong—hard.
B ₄ alite.....	Warped—cracked—rather weak—partly adhered.

From Table V it will be seen that the A₁ sample of elite behaved like a sound cement. The lack of soundness in the B₄ alite shows the presence of some free calcium oxide. The mixtures of celite and MgO set like a normal cement, but the expansion of the MgO caused the pat to go to pieces on steaming. This is no proof of unsoundness in the celite, for a pat of normal Portland cement and hard-burned MgO behaved

similarly. The question of the soundness of celite on steaming is therefore unsettled.

Some interesting facts seem to be brought out by the tables of analyses and molecular ratios. *First*, that although the proportion of ferric oxide, Fe_2O_3 , to the alumina, Al_2O_3 , is a little higher in the celite than in the alite, the difference is not very marked and the assumption that ferric oxide is molecularly equivalent to alumina, so far as the formation of celite goes, seems justifiable although the hydraulic properties of the aluminates and ferrites differ in degree. *Second*, Unger's contention¹ "that the alite contains the bulk of the alumina, if not all of it, while the celite contains all of the iron," is not sustained. *Third*, with a given basicity of the mass as a whole, the proportion of silica to alumina and ferric oxide in the celite increases with the temperature. *Fourth*, with a given temperature, the proportion of silica to the alumina and ferric oxide in the celite decreases as the basicity of the mass as a whole increases. *Fifth*, while, with a given basicity of the mass as a whole, the proportion of alumina and ferric oxide to the silica in the alite seems to increase somewhat with the temperature, this is open to some question, as the apparent increase may have been due to less complete removal of the celite. It is worthy of note that the proportion of ferric oxide to alumina holds fairly constant. *Sixth*, with a given temperature, the proportion of alumina and ferric oxide to the silica in alite decreases as the basicity of the mass as a whole increases. Since the celite must have been quite fluid at the temperature of absorption it would, like ordinary liquid solutions, be homogeneous at a given temperature and with a given basicity of the mass as a whole.

As a result of consideration of the experimental work herein described, the following hypothesis of the changes taking place above 1400° during the clinkering process and the constitution of the final clinker is suggested. *First*, that celite consists essentially of a calcium aluminate fusible a little above 1400° and capable of dissolving, when liquid, calcium orthosilicate and calcium oxide, this latter being the more readily soluble and that the solubilities of the orthosilicate and the calcium oxide follow laws parallel to those which govern the solubility of salts in liquid solution. No evidence is yet forthcoming to enable the chemical constitution of the pure, fusible aluminate to be given so that no chemical formula is suggested for it. *Second*, that alite consists essentially of either α or β' calcium orthosilicate holding in solid solution calcium oxide with some calcium aluminate and ferrite. The concentration of the calcium oxide held in solid solution is dependent upon the basicity of the mass as a whole and the temperature; but the limit of solubility apparently is when the proportions required to form the usually accepted tricalcic silicate have been reached. It has been shown by A. H. White, working in this laboratory,² that in the presence of a small amount of alumina calcium oxide could be made to apparently com-

bine with silica, SiO_2 , up to almost the amount required to form tricalcic silicate, and this work was confirmed by Shepherd and Rankin.³ The fact that in alite the amount of calcium oxide in excess of that required to form orthocalcium silicate is a function of the total basicity and that when alite reacts with water dicalcic silicate and calcium hydroxide are the first products of reaction, would suggest the conception that the calcium oxide in excess of that required to form calcium orthosilicate is in solid solution rather than in direct combination with the silica.

The above conception of the constitution of celite and alite would reduce the problem of the constitution of Portland cement clinker to a study of solubilities and would offer a comparatively simple explanation of the changes taking place at temperatures exceeding 1400° . A little above 1400° the calcium aluminate melts and simultaneously dissolves calcium oxide and calcium orthosilicate. As the transformation of the β or possibly γ orthosilicate into the α form progresses at temperatures above 1410° the solution of the α orthosilicate in the calcium aluminate would soon become supersaturated so that crystals of α orthosilicate containing calcium oxide and calcium aluminate in solid solution would begin to separate out. This process of transformation of the β or γ into the α orthosilicate would go on until the recrystallization of this latter into alite was complete. A certain minimum concentration of calcium oxide in solid solution in α orthosilicate seems to be necessary to prevent the transformation of the α into the β or γ forms just as the presence of certain concentrations of nickel or some other elements in iron will prevent the transformation of the γ into the α form of that element.

Although much work yet remains to be done it has been thought that the suggestion of a working hypothesis based upon the parallelism which seems to exist between fused solutions at high temperatures and aqueous solutions at ordinary temperatures might be of some service in the attempts which are being made to solve the difficult problem of the constitution of Portland cement.

CHEMICAL LABORATORY
UNIVERSITY OF MICHIGAN
ANN ARBOR

THE DRYING RATES OF RAW PAINT OILS—A COMPARISON

By L. V. REDMAN, A. J. WEITH AND F. P. BROCK

Received June 3, 1913

The object of this research is to compare the relative drying qualities of a series of raw oils used in the paint and varnish industry. Some of these oils, to the trade such as soya bean and fish oil, have been introduced in large quantities recently.

The oils used in this research are linseed, fish, soya bean and chinawood. Considerable work has been done upon the drying of linseed oil, and very recently investigations have been made upon suitable driers for fish, soya bean and chinawood oil, but no compari-

¹ *Cement and Engineering News*, Aug., 1910, p. 328.

² *THIS JOURNAL*, 1, 7 (1909).

³ *THIS JOURNAL*, 3, 211 (1911).

son has been made of the drying phenomena of these oils in the raw state, *i. e.*, without driers.

The authors hope to follow up this work and compare the relative drying and lasting qualities of the oils when standard driers are added.

HISTORICAL

Lippert¹ has found that raw linseed oil, when spread in thin films upon sheet iron, "increases in weight slowly for three days, more quickly on the fourth and becomes dry on the seventh. The total gain in weight is found to agree with that of Mulder, namely, 12.4 per cent. . . . Linseed oil, strongly boiled without driers, dries more slowly than raw oil, and is more difficult to manipulate owing to its great viscosity, but eventually it absorbs within 2 per cent of the oxygen taken up by the raw product."

Olsen and Ratner² found that linseed oil increased in weight 18.05 per cent when exposed in a thin film upon glass wool, in a stream of purified air passing at the rate of 15 liters a day for seventy-four days. They collected the water and carbon dioxide and volatile organic matter given up by the oil, and found that 14.55 per cent of water and 5.21 per cent of carbon dioxide were given off. This makes the total oxygen absorbed by the oil amount to 37.80 per cent.

Sabin³ found that raw linseed oil, without driers, increased in weight to a maximum (16-18 per cent) in seven days. This time of maximum increase agrees with the time of setting up, as given by Lippert. Sabin, however, states that the oil did not set up until after this point was reached.

Orloff⁴ found that linseed oil increases in weight 15-16 per cent with initial setting up at 12 per cent, when the oil is spread out into films, weighing 0.1-0.15 gram, over an area of 108 square centimeters.

Geuther⁵ found that linseed oil absorbs 23 per cent oxygen at room temperature in the dark, 34.7 per cent at 95° in light of Uviol-lamp and that the volatile products amount to 15 per cent by weight of the oil.

These investigations indicate that linseed oil films increase in weight from 8 per cent to 18 per cent with the absorption of oxygen; the maximum increase is reached about the seventh day; the setting up begins simultaneously with the maximum increase in weight; the volatile products given off consist mostly of water and carbon dioxide and amount to 15-20 per cent.

Meister⁶ states that chinawood oil is slower than linseed oil in absorbing oxygen and "although a skin is formed upon raw tung oil within one or two days, it is soft and non-elastic and not until after five or six days does it become firm like linoxyn."

DRYING MACHINE

The apparatus for drying (Plates 1 and 2, Figs. 1 and 2) consisted of a motor, a Sturtevant pressure blower, and a main equalizing chamber fitted on the

side with twenty small shelf boxes for holding individual plates. The motive power was supplied from the power circuit during the day and a storage battery at night. The fan was belted to the motor.

Fresh air was brought in from the outside through a 5-inch galvanized pipe in which were placed at two-foot intervals three cheese-cloth filters for removing dust, etc. Each filter consisted of three layers of

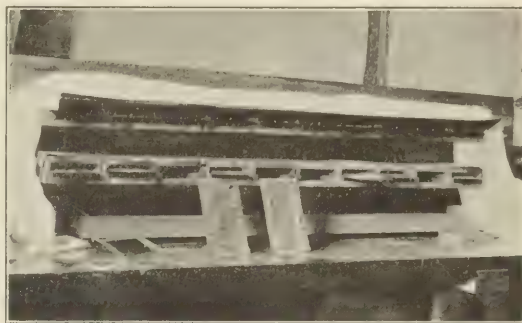


PLATE 1

cheese-cloth. The open ends of the individual boxes were covered with two thicknesses of cheese-cloth to prevent the entrance of insects. Plate 1 shows the arrangement of this curtain.

The equalizing chamber and individual boxes were constructed of white pine. Fig. 1 gives the dimensions of the equalizing chamber and Fig. 2 the dimensions of the individual drying boxes. The interior of the apparatus was coated with melted paraffin and by this means was made air-tight, dust- and water-proof. The outside of the box was given one coat of a quick-drying varnish.

The individual drying boxes were glued into slots cut into the side of the equalizing chamber in such a manner that the oil plates were perfectly level. Consequently the oil remained distributed in a uniform film over the plate, with no tendency to flow in any direction.

The air was admitted from the equalizing chamber

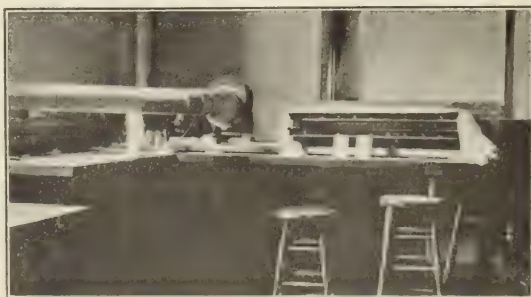


PLATE 2

into the individual drying boxes through a slot ($2\frac{1}{2}$ inches by $\frac{1}{8}$ inch, see Fig. 2). Care was taken to place the slot midway between the top of the box and

¹ *J. Frank. Inst.*, **1899**, August, p. 156.

² *J. Soc. Chem. Ind.*, **31**, 937, (1912).

³ *This Journal*, **3**, 84-86 (1911).

⁴ *Chem. Soc. Abstr.*, **1912**, **1**, p. 158.

⁵ *Chem. Abstr.*, **1**, 912 (1907).

⁶ *J. Soc. Chem. Ind.*, **30**, 95 (1911).

the plate; the drying box was made one inch wider than the plate to give uniform air distribution and to allow ready removal of the plates.

The velocity of the air current in the individual boxes was approximately ten miles per hour. The

stein & Company, New York; Marden, Orth & Hastings, Chicago; Alden S. Swan & Company, New York; and Frank L. Young & Kimball, Boston.

These samples of oils were recommended as pure and unadulterated. The constants, as determined by

Oil-Drying Machine.

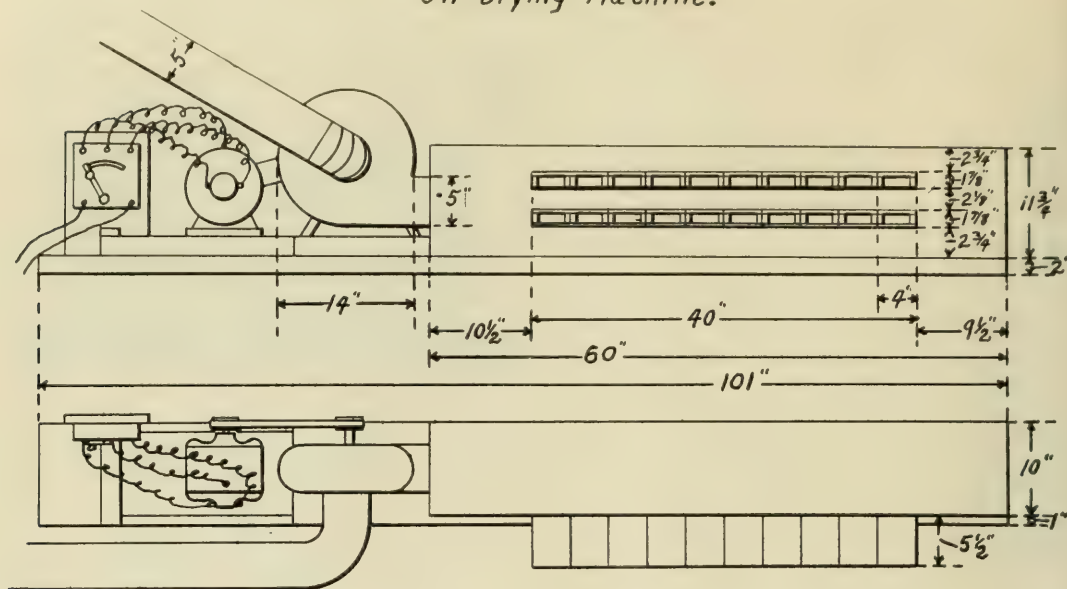


Figure 1.

total quantity of oxygen which passed over the films was 7,000,000 times that absorbed by the oil.

Any precautions taken to prevent irregular air currents were probably unnecessary, since the oxygen is so greatly in excess of that absorbed by the oil.

The machine was placed in a room where only diffused sunlight entered. Light entered the drying boxes through a curtain made of cheese-cloth.

WEIGHING THE PLATES

The plates were removed every morning from the drying boxes and weighed immediately without the use of a desiccator, on a balance sensitive to $\frac{1}{10}$ milligram. The weighings were carried out by removing the supporting tins (D, Fig. 2) from the boxes, lifting one edge of the glass plate (E, Fig. 2) with a knife point and inserting underneath a rubber covered two-pronged wire fork (Plate 1), by which means the plate could be lifted and transferred directly to the balance without coming in contact with the hands.

OILS

The samples of oils in this research were obtained through the kindness of the American Linseed Company, Chicago; The Chicago Varnish Company, Chicago; L. C. Gillespie & Sons, New York; A. Klip-

us, were in close agreement with the constants furnished by the companies' laboratories.

HISTORY OF OILS

Nos. 1 and 2, Linseed Oil. The oils were obtained from the same seed: No. 1 by the cold naphtha process and No. 2 by the hydraulic pressure method. The seed was grown in Southern Minnesota, and yielded 35.86 per cent oil and 9.15 per cent moisture. The oil content of the seed was below normal because of the extreme weather conditions.

No. 3, Menhaden Fish Oil. No history furnished.

Nos. 4, 5 and 6, Fish Oils. Sample 4 was winter-pressed fish oil which had been chilled, and grained after which the stearin was pressed out. Sample 5 was white Menhaden fish oil, which had been put through the same process as Sample 4, then bleached and repressed after bleaching. Sample 6 was bleached fish oil which had been chilled, grained, settled, pressed and bleached.

No. 7, Soya Bean Oil. The sample was English soya bean oil which had been extracted from the beans by the naphtha or cold-pressed process.

No. 8, Soya Bean Oil was produced by the cold process at Hankow.

No. 9, Chinawood Oil was obtained by the cold process at Hankow from chinawood nuts.

No. 10, Chinawood Oil was the average Hankow variety.

DESCRIPTION OF THE CURVES

Fig. 3 shows the increase in weight of the several oils expressed in per cent gain in weight as ordinate and time in days as abscissa. Each curve represents the average of two or four films. In all the experiments the duplicates were in very close agreement.

Details of Drying Box.

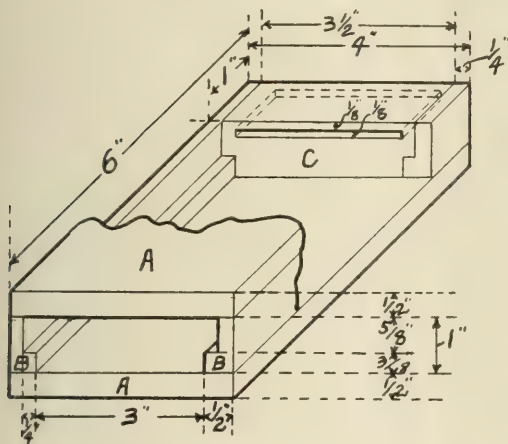
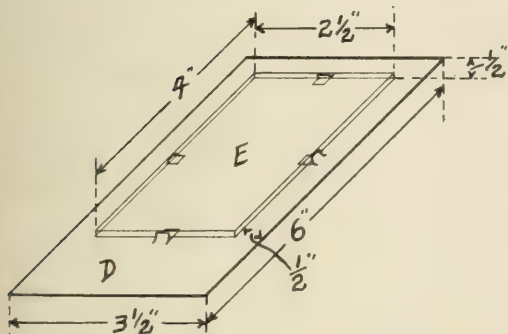


Figure 2.

Details of Drying Plate.



Linseed oil No. 1, Curve 1, began to increase in weight at the end of the first day. The first sample reached its maximum increase (13 per cent) on the seventh day. Both samples set up into tough transparent films. They can not be marred by the finger tip, but are easily scratched with the finger nail.

Both films had a slight odor of linseed. Curves for Linseed Oil No. 2 were similar to Linseed Oil No. 1.

Menhaden Fish Oil, No. 3, Curve 3. The increase in weight was very rapid at the beginning of the experiment, 6.5 per cent being absorbed at the end of the first day and a maximum increase in weight of 11 per cent was reached at the end of the fourth day. A continual decrease is shown from the fifth to the twentieth day. An irregularity is noticed in the curves between the seventh and eighth days on all the fish oils (Curves 3-6). This was the highest temperature (86° F.) reached during the experiment and the lowest humidity (54%).

The fish oils lose most of their odor after two days drying. The films are yellowish in color, easily marred by the finger tips and are very soft, stringy and sticky after the 20 days. They showed no signs of setting up to a solid film beyond a thickening of the oil.

Menhaden Fish Oil No. 4, Curve 4, is very similar to those of Fish Oil No. 3, but the maximum gain in weight is 2 per cent greater, being 13.5 per cent. The films are more viscous than No. 3. The color is slightly yellowish.

Fish Oil No. 5, Curve 5, follows closely the two fish oils already described and shows a maximum gain of 13 per cent at the end of the third day. At the end of the experiment, the properties of the films were the same as of No. 4. The films are yellow and transparent.

Fish Oil No. 6, Curve 6, follows the same general form as those of the other fish oils and shows a maximum gain of 13.5 per cent at the end of the third day. The properties of the films at the end of the test are similar to Nos. 4 and 5.

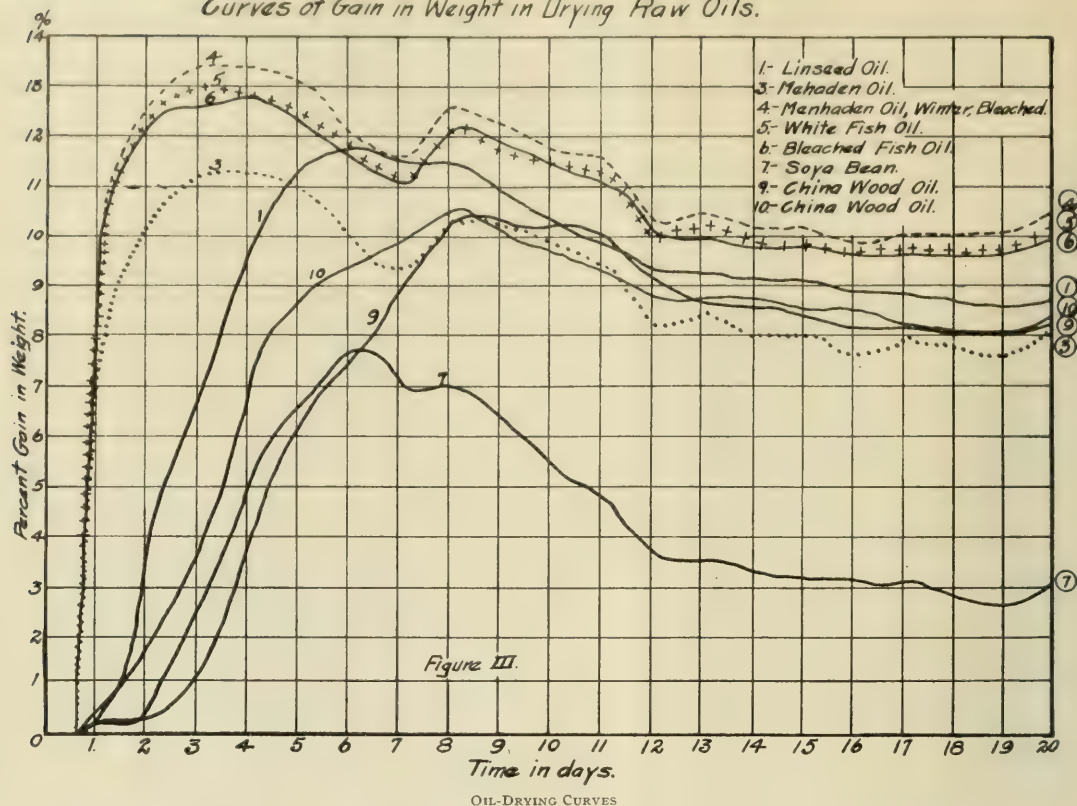
Soya Bean Oil No. 7, Curve 7, shows a slow increase (2 per cent) the first two days; a rapid increase (6 per cent) for the third and fourth days; the maximum increase of 9 per cent at the end of the sixth day. A general decrease then followed to the end of the 20 days. The films set up in fair shape, although a little more sticky and less tough than the linseed oils. The films are a very beautiful, light, transparent color.

Soya Bean Oil No. 8 was similar to Oil No. 7.

Chinawood Oil No. 9, Curve 9, shows very little increase in weight for the first three days. On the third day the oils began to show a characteristic translucent whitening simultaneous with a rapid increase in weight. The increase reached its maximum of 10.7 per cent at the end of the ninth day and the weight of the films decreased from that time to the end of the experiment on the twentieth day. The films at the end of the experiment were translucent white with a frosty appearance and have a wood oil odor. When rubbed between the fingers they are of a mealy nature like art gum. They are not easily scratched by the finger nail and are not sticky or tacky.

Chinawood Oil No. 10, Curve 10, has the same general characteristics as Curve 9. One difference was noticeable: the oil began to whiten at the end of the second day and a rapid increase in weight was also noticeable. The maximum increase (10.5 per cent) in weight was reached at the end of the ninth day and

Curves of Gain in Weight in Drying Raw Oils.



from that time the decrease was continuous to the end of the experiment. The conditions of the films were about the same as for Oil No. 9.

DAILY VARIATION CURVES

The daily variation curves (Fig. 4) were plotted for per cent increase in weight per day giving the time in days as the abscissas and the per cent variation in weight as the ordinates.

The average temperature and humidity curves were also plotted in Fig. 4. The abscissae are given in days and the ordinates shown on the right side of the figure are given in degrees Fahrenheit for temperature and humidity expressed in per cent of saturation, the object being to detect, if possible, some relation between the rate of drying of the oil, the temperature and the humidity.

No general conclusions can be drawn as to the effect of humidity and temperature from these curves. The only noticeable irregularity which can be explained by humidity is in the fish oil curves on the ninth day. There is a noticeable increase in each of the eight samples, about 2 per cent, when the humidity had increased 30 per cent. This agrees with what has been noticed by previous investigators that fish oils are hygroscopic in warm, moist air.

The curves show that the linseed oils were increasing in weight most rapidly on the fourth and seventh days. The eight samples of fish oil increased in weight very rapidly for the first two or three days; the soya bean oil samples increased most rapidly on the fifth day and the four samples of chinawood oil increased most rapidly on the fourth and fifth days. None of the samples of the oils showed any marked decrease in weight from the fourteenth to the twentieth day.

CONDITION OF FILMS

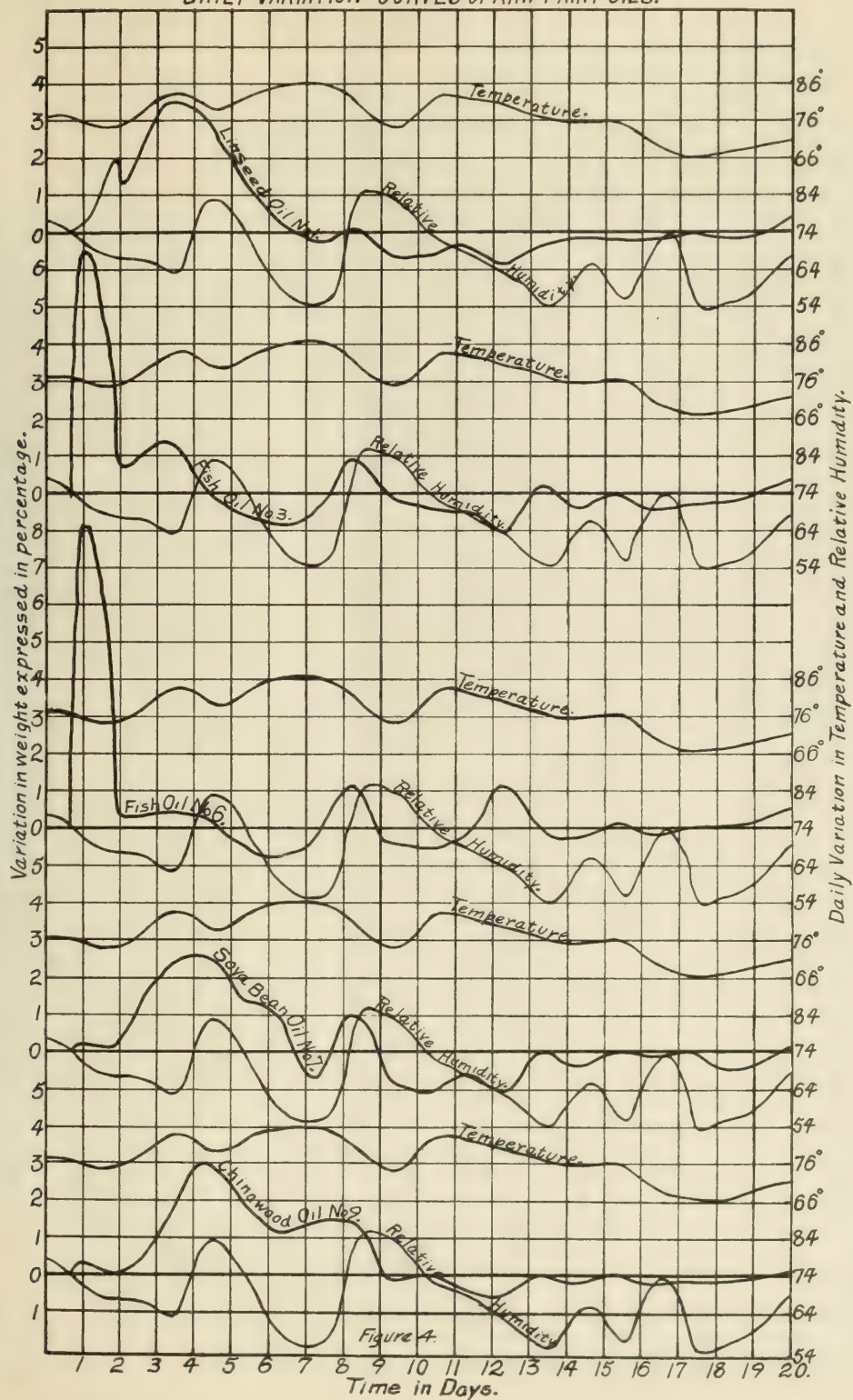
The oils had not begun to set up except the china-wood oil at the end of the fifth day, at which time most of the oils had absorbed the maximum amount of oxygen. This has already been noticed by Sabin.¹ He has also noted a break in the curve representing the loss in weight, after the film has reached its maximum increase. This break is at the fifteenth day for one set of curves and the tenth day for the second set. In our curves a similar break is shown on the thirteenth day. This break is probably due to a point being reached at which the loss of volatile products just equals the gain by oxidation.

SUMMARY

1. At the end of the twenty days the raw linseed

¹ THIS JOURNAL, 3, 84 (1911).

DAILY VARIATION CURVES of RAW PAINT OILS.



oils had set up to a dry, tough transparent film which could be scratched by the finger nail.

2. The raw fish oils did not set up like a drying oil, but remained a sticky viscous, transparent yellowish liquid with a very slight fish oil odor.

3. The raw soya bean oils set up to a transparent film. The film was much lighter in color, but was not equal to linseed oil in toughness.

4. The raw chinawood oils gave excellent films: their surface, however, was dull and frosted.

5. It was very noticeable in the drying of the chinawood oils that the frosted surface began to appear simultaneous with the rapid increase in weight of the film which reached its maximum simultaneous with the complete frosting.

6. The raw fish oils gained weight much more rapidly than any of the other oils and the total gain was greater, the average maximum gain being about 12.5 per cent. The linseed oils were next in order, both in the rate and the amount (11.5 per cent) absorbed.

Raw chinawood and soya bean oils increase in weight at about the same rate, but more slowly than raw fish and linseed oils. The maximum gain (10.5 per cent) for chinawood oils is 1 per cent less than that of linseed oil and the maximum gain (7.7 per cent) for soya bean oil is 2.8 per cent less than that of chinawood oil.

7. Linseed, chinawood and soya bean oils dry within twenty days to a solid film without the addition of artificial driers.

8. All the fish oil samples remained tacky, viscous liquids after twenty days of drying.

DEPARTMENT OF INDUSTRIAL RESEARCH
UNIVERSITY OF KANSAS
LAWRENCE

THE GASES FORMED IN ANAEROBIC SEWAGE DECOMPOSITION¹

By R. H. JESSE, JR.

Received April 23, 1913

In the fall of 1909 a gas explosion occurred in one of the septic tanks at Highland Park, Illinois. The State Water Survey made an investigation of the tank in order to determine, if possible, the causes that led to this explosion. In the course of the investigation, samples of the gas evolved were collected from the tank in question, as well as from another of the Highland Park tanks, which had been working satisfactorily. The composition of the two samples was compared with that of two samples collected from the Urbana septic tank. The composition of the gas, however, furnished no adequate explanation of the cause. It may be recalled that a similar explosion in the Saratoga tank several years ago was much discussed at the time.²

It was interesting to compare the composition of these four samples with that of similar gases analyzed

by other observers. A search of the literature revealed only the few analyses given in Table I:

TABLE I—ANALYSES OF SEPTIC TANK GASES

Source	Gas absorbed						Analyst or authority	
	CO ₂	O ₂	carbons hydro-	by Cu ₂ Cl ₂	CH ₄	H ₂		N ₂
Exeter, England...	3.9	22.7	4.8	2.2	66.1	Dibdin (a)
Exeter, England...	3.5	8.0	40.1	6.2	42.2	
Manchester, Eng-land...	0.6	24.4	36.4	38.6	Rideal (a)
Lawrence, Mass...	6.0	73.0	5.0	16.0	Fowler (b)
Worcester, Mass:	3.4	0.5	0.3	0.6	78.9	...	16.3	Gill (c)
October.....	5.6	1.9	...	0.8	75.3	...	16.4	Kinnicutt and Eddy (d)
November.....	4.1	1.2	...	0.5	76.9	...	17.3	
December.....	2.5	2.0	...	0.4	69.5	...	25.6	Eddy (d)
March.....	8.8	1.0	...	0.1	13.5	...	76.8	
April.....	9.8	0.9	...	0.2	28.4	...	60.7	Kinnicutt and Eddy (d)
May.....	15.2	1.5	...	0.1	26.9	...	56.3	
June.....	17.0	1.2	...	0.2	52.1	...	29.5	Kinnicutt and Eddy (d)
July.....	8.7	1.3	...	0.4	63.8	...	25.8	
September.....	8.0	1.6	...	0.4	57.8	...	32.2	Kinnicutt and Eddy (d)
October.....	6.9	0.6	...	0.6	72.4	...	19.5	
November.....	6.3	0.7	...	0.3	79.2	...	13.5	Kinnicutt and Eddy (d)
December.....	5.6	0.9	...	0.1	76.8	...	16.6	
Mean.....	8.2	1.2	...	0.34	57.7	...	32.5	

(a) Rideal, "Sewage and the Bacterial Purification of Sewage," 3rd. Ed., p. 97.

(b) Annual Report Rivers Dept., Manchester, 1901.

(c) Report Mass. State Board of Health, 1899, p. 422.

(d) Sewerage Commission, Connecticut, Third Report, 1901.

The samples collected in Illinois differed considerably from the Worcester samples. This was especially true with respect to the nitrogen and carbon dioxide content. There were still wider variations when comparison was made with the English samples. Therefore, it was thought worth while to make a more extended study of the gases of Illinois tanks, in order to determine whether these differences were constant, and if so, whether they were indicative of any difference in the decomposition processes. In the summer of 1911, gases were collected from tanks at the places in Illinois indicated in Tables II and III. This report presents the analyses of these gases with a discussion of the results.

The outfit used in collecting the samples is shown in the accompanying cut. A ten-inch glass funnel was connected by rubber tubing to a 500 cc. cylindrical glass container fitted at each end with a well-ground glass stopcock. The other end of the container was connected by means of a rubber tube to a glass tube which ended in a ground glass check-valve. This tube passed through a rubber stopper to the bottom of a stout glass bottle. Another tube which ended flush with the bottom of the stopper led from this bottle to a bicycle pump in which the leather plunger had been reversed so that the up-stroke caused the suction. The manner of operation is as follows: the top layer of sludge of a septic tank is broken and the funnel is dropped into the water. The pump is started and pumping is continued until the funnel, the connecting tubes, and the gas container are completely filled with water, and enough water has entered the bottle to seal the end of the longer tube. A disc of copper gauze fastened into the funnel with sealing-wax serves to filter out solid particles which might cause clogging of the tubes. When the apparatus is full of water the stopcocks are closed.

¹ Abstracted by the author from a report published in University of Illinois Bulletin, Water Survey Series No. 9.

² Mason, Jour. N. E. Water Works Assoc. The possibility of the presence of a spontaneously inflammable gas was debated. In this connection it is interesting to note that in 1851, Scanlan and Anderson reported phosphuretted hydrogen as a constituent of sewer air. They, however, give no details of their method of testing for this gas. *J. Chem. Soc.*, 3, 13 (1851).

Where there is a good layer of sludge on the bottom of the tank, gas is generally trapped in this layer. By stirring this sludge with a pole, the gas rises and is caught under the funnel. Where there is not sufficient sludge on the bottom to hold the gas, samples may be collected generally by raising the funnel somewhat and moving it cautiously around under the unbroken

hydrogen was separately determined by absorption with palladium sponge. The palladium tube was tested constantly during the work. This is an important point because no hydrogen was found in any of the gases tested, although its presence is reported by other investigators.

Nitrogen is usually determined by difference. The accumulated errors of the analysis thus fall upon this constituent. Because one of the principal differences between the gas samples first collected lay in the nitrogen content, it was thought worth while to determine the nitrogen as well as to calculate it by difference. This was accomplished by keeping an account of the amount of nitrogen introduced with the air and oxygen used for the combustion and by absorbing the excess oxygen after the combustion. The nitrogen found in these two ways agreed in a manner which must be considered satisfactory when the errors affecting the determination by difference are considered.

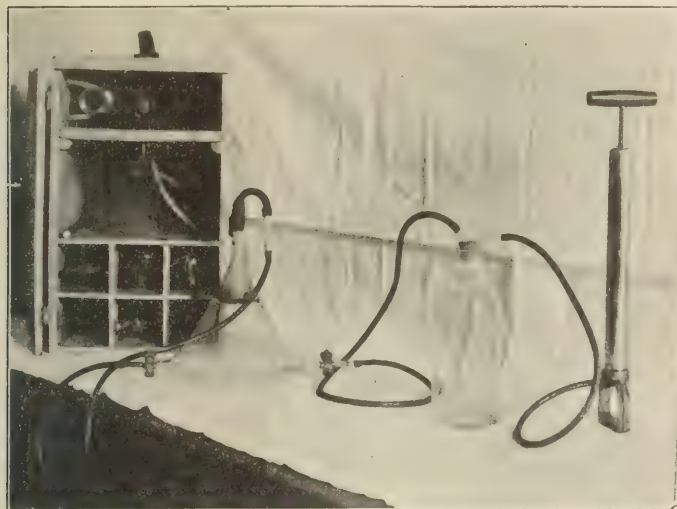
Since any hydrogen sulfide present had been absorbed with the carbon dioxide, it was necessary to make a special test with a fresh sample of gas. It was found by blank tests that when 100 cc. of gas containing 0.05 cc. of hydrogen sulfide were passed through a very

faintly acid solution of cadmium chloride, the solution was colored yellow. This served as a qualitative test. If no coloration was produced under these conditions no hydrogen sulfid was reported. Where a qualitative test was obtained a quantitative determination was made by passing known quantities through a $N/50$ iodine solution and titrating with sodium thiosulfate.

In Table II are the results of the analyses made in this laboratory. These are shown graphically also in the figure.

The analyses are not directly comparable with those of Kinnicutt, because his collections were made from a closed tank from which there was no escape for a gas except by solution. Our samples, however, in addition to the effect of solution, may have been affected by different rates of diffusion of the various constituents in their escape through the sludge.

In the summer of 1911, the Illinois river, which carries the sewage of Chicago, became highly polluted. Between the mouth of the Kankakee and Chillicothe there was some sludge on the river, much offensive odor, and a good deal of gas formation. The State Water Survey, in connection with the State Laboratory of Natural History, made dissolved oxygen determinations over this region. At the same time, samples of the gas were collected and analyzed. The results of these analyses are given in Table III. In order to compare these gases with those from stagnant pools, which are not polluted with sewage, there is given an analysis of a gas sample collected from



APPARATUS FOR COLLECTING GAS SAMPLES

layer of top sludge. In this case, however, care must be taken never to raise the funnel high enough to allow air to enter. This last method of collection is not to be recommended where the other method is practicable.

When the funnel is about two-thirds full of gas, the gas container is raised to a vertical position, the end which is attached to the safety bottle *downwards*, and by pumping, the water is drawn from the container into the bottle and the gas enters the top of the container. The above process is repeated until all the water has been pumped out of the container.

The analysis was carried out by the use of the regular Hempel apparatus. The burettes were water-jacketed and temperature corrections were made wherever they were necessary. Absorptions were made successively with caustic potash, alkaline pyrogallol, and ammoniacal cuprous chloride, followed by dilute sulfuric acid. No heavy hydrocarbons were ever detected.

The combustible gases were determined with the ordinary explosion pipette and by the Drehschmidt-Winkler heated platinum capillary tube method. Burettes filled with mercury were used for the combustion work, and much care was taken to avoid solution of the carbon dioxide formed. Neglect of these precautions can easily cause errors of several per cent. In general these errors are in such a direction that the calculated hydrogen content appears high. This point will be discussed again later. To make sure that no such errors affected the results of these analyses,

TABLE II

Lab. No.	Town	Gas absorbed					H ₂ S
		CO ₂	O ₂	by Cu ₂ Cl ₂	CH ₄	N ₂	
1	Urbana	10.83	0.1	0.7	81.03	7.34	..
3	Urbana	10.2	0.0	0.7	81.5	7.6	..
4	Urbana	10.2	0.11	0.22	85.10	4.37	..
28	Urbana	21.69	0.0	0.42	69.55	8.44	..
27	Urbana	11.36	0.05	0.50	83.4	4.79	..
26	Urbana	5.76	0.1	0.6	87.13	6.41	..
29	Urbana	5.89	0.5	0.22	87.36	6.23	..
56	Urbana	13.74	0.09	0.54	79.61	6.02	..
57	Urbana	9.11	0.09	0.60	84.73	5.47	..
58	Urbana	6.08	0.4	0.32	84.63	8.57	..
74	Urbana	23.57	0.13	0.0	73.3	3.0	..
75	Urbana	18.98	0.17	0.55	74.9	5.4	..
5	Champaign	27.1	0.08	0.05	71.43	1.34	..
6	Champaign	26.4	0.0	0.0	73.6	0.0	..
7	Champaign	28.18	0.1	0.2	71.52	0.0	..
12	Highland Park, Tank A	12.18	0.0	0.32	79.77	7.72	..
76	Highland Park, Tank B	8.44	0.13	0.0	89.5	1.8	..
8	Highland Park, Tank B	12.80	0.2	0.0	87.0	0.0	..
9	Highland Park, Tank B	13.7	0.2	0.45	86.1	0.0	..
77	Highland Park, Tank B	20.77	0.87	0.0	76.2	2.16	..
10	Highland Park, Tank C	23.3	0.0	0.0	69.93	6.77	..
11	Highland Park, Tank C	17.3	0.0	0.0	78.0	4.7	..
16	Chicago, Tank A, open septic	8.60	0.0	0.30	84.92	6.18	..
17	Chicago, Tank B, closed septic	6.99	0.0	0.46	84.2	8.3	0.04
18	Chicago, Tank B, closed septic	5.17	0.32	0.22	83.1	11.1	0.09
19	Chicago, Tank C, settling tank	9.31	0.62	0.45	83.9	5.72	..
20	Chicago, Dortmund tank	6.42	0.30	0.0	60.0	33.06	0.22
30	Winnetka	13.81	0.0	0.45	82.35	3.39	..
31	Winnetka	11.13	0.0	0.32	86.25	2.30	..
32	Winnetka	3.1	0.0	0.55	92.77	3.58	..
33	Lake Forest	7.1	0.13	0.33	89.8	2.64	..
34	Lake Forest	10.00	0.36	0.98	85.77	2.89	..
64	Woodstock	21.40	0.0	0.70	77.36	0.54	..
66	Woodstock	20.22	0.0	0.50	78.48	0.80	..
65	Woodstock	3.79	0.25	0.53	89.54	5.89	..
40	Downers Grove	26.28	0.0	0.4	73.32	0.0	..
14	Downers Grove	16.15	0.11	0.53	83.2	0.01	..
39	Downers Grove	17.07	0.0	0.30	82.63	0.00	..
25	LaGrange	7.31	0.0	0.37	80.81	11.51	..
37	Naperville	19.06	0.0	0.1	74.5	6.34	..
38	Naperville	13.04	0.62	0.18	77.52	8.64	..
36	Naperville	14.19	0.09	0.95	77.65	7.12	..
63	Wheaton	9.33	0.0	0.72	82.10	7.85	0.04
62	DeKalb	30.52	0.0	0.59	68.89	0.0	..
59	DeKalb	22.24	0.05	0.95	75.37	1.39	..
60	DeKalb	29.06	0.00	0.56	70.46	0.0	..
61	DeKalb	32.00	0.13	0.72	66.93	0.22	..
47	Collinsville, Tank I	10.54	0.37	0.26	84.40	4.00	0.43
50	Collinsville, Tank I	17.98	0.23	0.34	81.26	0.00	0.19
49	Collinsville, Tank I	21.08	0.07	0.56	75.16	3.13	..
48	Collinsville, Tank II	9.46	0.09	0.65	86.00	3.80	..
51	Edwardsville	11.33	0.15	0.21	87.34	0.97	..
23	Worcester, Mass.	52.15	0.0	0.0	34.76	13.09	..
52	Worcester, Mass.	47.04	0.0	0.0	45.46	7.5	..
41	Columbus, O., secondary	8.11	0.0	0.1	83.5	9.29	..
42	Columbus, O., secondary	8.55	0.07	0.20	86.99	4.19	..
43	Columbus, O., primary	13.48	2.07	0.0	67.46	16.99	..
44	Columbus, O., primary	15.17	0.1	0.0	79.43	5.30	..
45	Columbus, O., Imhoff	14.45	0.05	0.0	80.13	5.37	..
46	Columbus, O., Imhoff	13.39	0.61	0.34	81.03	4.63	..

TABLE III

Lab. No.	Town	Gas absorbed					
		CO ₂	O ₂	by Cu ₂ Cl ₂	CH ₄	N ₂	H ₂ S
53	Illinois River, Morris	19.45	0.0	0.69	79.30	0.56	..
54	Illinois River, Morris	19.31	0.0	0.32	79.51	0.86	..
55	Illinois River, Morris	18.12	0.09	0.68	78.91	2.14	..
60	Illinois River, Morris	21.49	0.0	0.30	73.00	5.21	..
70	Illinois River, Morris	23.85	0.00	0.19	75.96	0.0	..
67	Ill. R. above dam, Marseilles	18.74	0.0	0.0	81.28	0.0	..
68	Ill. R. above dam, Marseilles	16.85	0.05	0.55	82.55	0.0	..
71	Ill. R. above dam, Henry	17.76	0.0	0.52	80.83	0.89	..
72	Ill. R. above dam, Henry	11.99	0.44	0.42	61.91	25.24	..
82	Ill. R. above dam, Marseilles	4.65	0.1	0.30	93.99	0.91	..
83	Ill. R. above dam, Marseilles	14.60	0.1	0.75	83.45	1.1	..
81	Mazon Creek	0.75	0.66	0.55	56.44	41.61	..

from the Illinois River is as striking as is the similarity between the latter and the gases from septic tanks.¹

"Rideal" has made the following classification of the chemical processes of the septic tank:

1. An hydrolysis of complex albuminous bodies, which takes place in two stages; (a) conversion to a soluble form, peptonization; (b) hydrolysis of the peptones into amino acids, leucin, tyrosin and aromatic bodies. This process involves no gas formation.

2. Splitting up of the amino acids into fatty or aro-

¹ These gases should be compared with those from the Spree and the Seine. (Spitta, *Archiv für Hygiene*, **38**, 276ff.) The amounts of carbon monoxide and hydrogen sulfide reported are astonishing.

² "Sewage and the Bacterial Purification of Sewage," 3rd Ed., p. 105f.

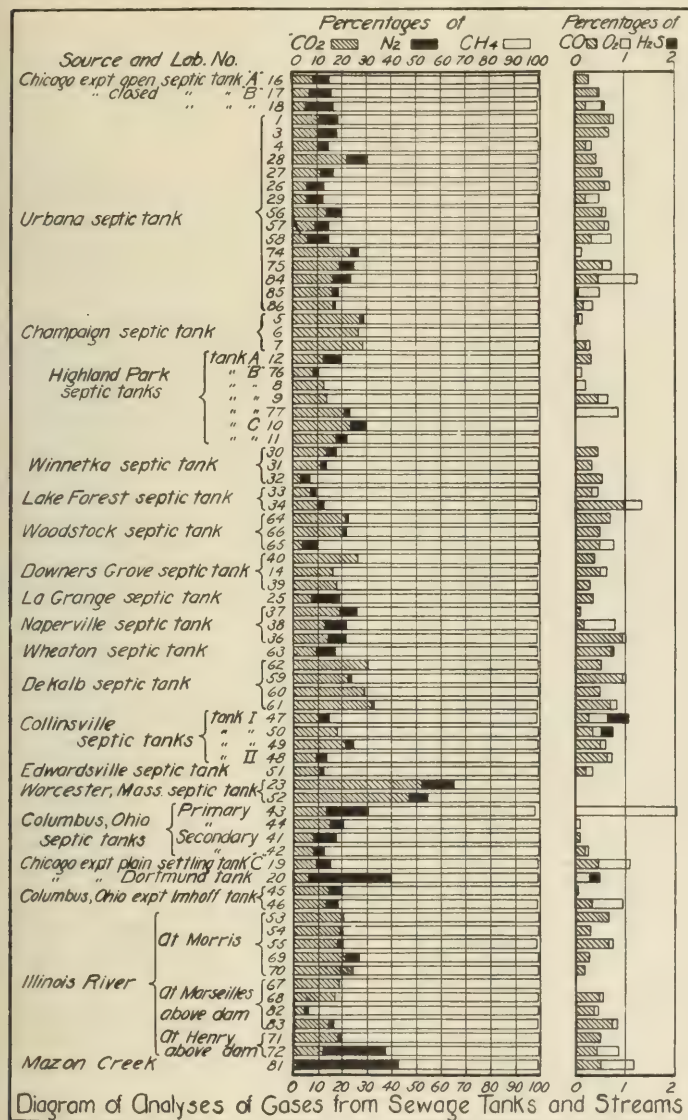
Mazon Creek, which enters the Illinois River near Morris. The difference between this gas and those

matic acids, with the formation of ammonia or nitrogen or both together.

3. The acids formed by the split of the albumin molecules break down into still simpler acids. In this process, hydrogen and methane are generated.

8. The formation under the influence of bacteria of hydrogen sulfide and mercaptans from the sulfur in the organic molecule.

Carbon dioxide is the result of the breaking down of the complex organic acids, and of the decomposition of cellulose and carbohydrates.



curs makes it difficult to obtain enough for thorough investigation.¹

Ammonia.—Frequent tests with dilute acid showed that no ammonia was present in the gases. It is certain that ammonia is formed in the septic action, but apparently it all remains in solution.

Hydrogen.—Careful tests with palladium sponge furnished evidence that there is no hydrogen in any of the gases. Kinnicutt reached this same conclusion in regard to the gas from the experimental tank at Worcester. Other investigators have, however, reported hydrogen. In this part of the gas analysis it is extremely easy to make errors which would make it appear that hydrogen is present. For the combustion, an aliquot portion of the residue is taken to represent the whole. There is in addition a multiplication of the analytical error in the calculation, so that an actual error of 0.2 cc. may be magnified very easily to several per cent of the whole. It is, thus, quite probable that in most of the cases where small amounts of hydrogen have been reported this is due to faulty analysis. On the other hand, it seems hardly possible that the 36 per cent of hydrogen from Exeter reported by Rideal can be due to error.

There is no doubt that hydrogen can be formed as a product of many of the reactions described by Rideal. Thus, in the fermentation of the amino acids and of the fatty acids, we have the formation of hydrogen. In the decomposition of cellulose, hydrogen or methane may be evolved according to the type of bacteria causing the hydrolysis. Frankland² has found that dulcitol, when fermented in a peptone broth under the influence of *B. ethaceticus*, gives off gases which vary from 27 to 60 per cent CO₂, and from 39 to 48 per cent H₂. Similar results were obtained for mannitol. Pakes and Jollyman³ have found that the gases evolved by *B. pyocyaneus* and *B. coli communis* consist of carbon dioxide and hydrogen and nitrogen, if nitrates are present. The gases formed by the action of *B. tetani* are hydrogen and carbon dioxide. We have made analyses of two samples formed by *B. coli communis* in a peptone broth containing sugar. The conditions were anaerobic. The results of these analyses are:

	CO ₂	O ₂	CO	CH ₄	H ₂	N ₂
I.....	36.47	0.4	0.72	0.99	59.62	1.80
II.....	31.63	0.3	0.72	0.93	64.18	2.96

This is in fair agreement with the work of Pennington and Küssel,⁴ who report 62–70 per cent H₂, 23–34 per cent CO₂, and 1–4 per cent CH₄. They further state that methane is not formed when oxygen is excluded.

It is thus seen that under conditions apparently similar to those which hold in the septic tank, we may have the formation of hydrogen. Why is it, then, that no hydrogen has been detected in the American tanks? It would seem that this question is one for investigation.

Nitrogen.—Nitrogen results from the splitting of

the albumin molecules and the further hydrolysis of the amino acids resulting from this split. The hydrolysis can go on in two ways: (a) with the production of ammonia or amines; (b) with the production of free nitrogen. Which of these cleavages will occur is determined by the conditions of the reaction. As a matter of fact, both reactions generally go on simultaneously in the septic tank. The above results furnish, so far as we are aware, the first examples of gases in which free nitrogen is absent. Many other samples show very small quantities. The average for these Illinois gases is below 8%. The reason for this low nitrogen content is not apparent.

Ehrenberg⁵ has made some experiments on the evolution of nitrogen during the putrefaction of cow's urine and feces. In a first series of experiments he found no nitrogen formation either under aerobic or anaerobic conditions. In a second series, where the putrefactive processes were more intense, there was a formation of nitrates and an evolution of free nitrogen. Kellner and Yoshii⁶ have confirmed his work. They ascribe the formation of free nitrogen to secondary reactions. B. Tacke³ found no evolution of nitrogen when nitrates were absent, but such an evolution took place in the presence of nitrates. Pakes and Jollyman⁴ have found that nitrogen is generated under the influence of *B. coli communis* when nitrates are present. B. E. Dietzell,⁵ working on the putrefaction of blood and urine, found that the evolution of nitrogen depends on the formation of free nitrous acid which then reacts with leucine to form leucic acid, water, and nitrogen. Nitrous acid also attacks primary amines with the evolution of nitrogen. If chalk is present to neutralize the nitrous acid, the formation of free nitrogen is prevented.

It is perhaps not safe to draw too strict an analogy between these reactions and those that take place in the septic tank. All of the experiments just mentioned indicate that, for the formation of free nitrogen, there must be present some form of oxidized nitrogen. We could conceive of conditions in a tank which would prevent the formation of nitrates and nitrites. Then, according to the experiments, no nitrogen would be formed. The possibility is thus suggested that the amount of free nitrogen may give some indication of the completeness of the anaerobic condition of the tank. The results of Dietzell's experiments would also suggest that the amount of nitrogen generated might depend, to some extent, on the alkalinity of the sewage, and, therefore, in a less degree, on the character of the water supply.

Methane.—This gas was in all cases, except the gases from Worcester, Mass., the largest single constituent.

Hydrogen Sulfide.—Miller⁶ has isolated from the intestines an organism which causes decomposition of albumin with the generation of hydrogen sulfide. The *Bacterium sulphureum* has a similar action on albu-

¹ Zeit. physiol. Chem., **11**, 145–178.

² Ibid., **12**, 95–112.

³ J. Chem. Soc., **1889**, A, 738.

⁴ Loc. cit.

⁵ J. Chem. Soc., **1882**, A, 811, 1122.

⁶ Deutsche Medizinische Wochenschrift, **1889**, No. 49.

¹ Kinnicutt's blood spectrum and I₂O₅ tests also failed to give indications of carbon monoxide. Compare Spitta (foot-note, above).

² J. Chem. Soc., **1892**, 259; Proc. Chem. Soc., **110**, 70–72; **114**, 132 (1892).

³ J. Chem. Soc., **1901**, 322, 459.

⁴ J. Am. Chem. Soc., **22**, 556 (1900).

minoids. The *Bacterium hydrosulphureum ponticum* is able to reduce sulfates to sulfides. Beyerinck's¹ *Genus Aerobacter* forms hydrogen sulfide from proteids and other compounds of sulfur except sulfates. Balistreri² has found eighteen different bacteria which produce hydrogen sulfide. Neucki and Sieber³ have discovered hydrogen sulfide in the putrefaction products of serum albumin.

In spite of all this, hydrogen sulfide was found in four tanks only. Absence of hydrogen sulfide in the gases, however, does not prove that none was formed. Iron salts are an almost universal constituent of sewage, and these, of course, tend to remove the hydrogen sulfide as fast as it is formed.

It cannot be doubted that in some cases mercaptans are formed by sewage decomposition. All tests with isatin in sulfuric acid⁴ failed to give any indication of their presence in the gases.

The principal result of this study of the gas formed in anaerobic decomposition has been to raise several questions which will require further study before they can be answered. It has been suggested that the quantity of carbon dioxide evolved may run parallel to the amounts of cellulose and carbohydrates in the sewage, and that the amounts of this gas in different parts of the tank may serve as a measure of their rate of hydrolysis. The fact that no hydrogen is present in the gases has been confirmed. It has been pointed out that hydrogen may be expected as a product of many of the reactions which are supposed to take place. A study of the conditions which prevent the hydrogen formation is demanded. The conditions which prevent or reduce the disposal of nitrogen as free nitrogen are not clear. Dr. Bartow and his associates in the Water Survey intend to continue the work along these lines.

This work was undertaken for the Water Survey at the request of the Director, Dr. Edward Bartow. I am grateful for the interest he has shown in it, and for the help he has constantly given me during its progress. It is a pleasant duty, also, to acknowledge the efficient services of Mr. H. P. MacGregor, who helped me with the largest part of the work of collection and analysis.

CHEMICAL LABORATORY, STATE WATER SURVEY
URBANA, ILLINOIS

A MODIFIED FORM OF STABILITY TEST FOR EXPLOSIVES⁵

By H. C. P. WEBER

Sometime ago an investigation on the stability of nitrocellulose plastics was undertaken at the Bureau of Standards and the question of the stability of these materials at normal and elevated temperatures was one of the questions studied.

One of the stability tests employed in that investigation seems of sufficient interest to warrant calling attention to it, especially since it does not seem pos-

sible to carry the investigation further at present.

The papers to which reference has been made in connection with this subject are given below, and will not be cited again in detail.

There is perhaps no need for going into details regarding all the various tests proposed. While there are many of them, each having its own particular advantage, only a few are at all generally applied. The reason for adding to their number is that while this test is an explosion test, and therefore simple and rapid, it is in reality a determination of the change of decomposition velocity with rise in temperature and, as such, a measure of stability.

Various investigators have touched upon the influence of the rate of heating on the result, whether it be in the explosion tests or in methods depending on the amount or rate of gas evolution. For this reason the rate of heating in the explosion tests is defined within certain limits. The decomposition of nitrocellulose is autocatalytic, and when a certain surrounding temperature is attained, say 135° C., nearly all samples of nitrocellulose will explode if kept in surroundings of that temperature long enough. The temperature of the decomposing material may be a few or many degrees above 135°. In the investigation of nitrocellulose plastics we have repeatedly seen differences of 30° and 40° between the temperature of the surroundings and of the sample when the substance went off. The amount of this difference depends on the mass of the material and its heat conductivity, and on the heat conductivity of the system used for test. These factors enter into the German 135° test

¹ Aspinwall, "Stability Tests for Smokeless Powder and Nitro-explosives," *J. Soc. Chem. Ind.*, **21**, 687.

Bergmann and Junk, "Stability of Nitrocellulose," *Z. angew. Chem.*, **17**, 17, 982, 1018, 1074.

Cullen, "Note on the So-called 'Heat Test' for Explosives," *J. Soc. Chem. Ind.*, **20**, 8.

Escales, "Stability of Nitrocellulose," *Z. angew. Chem.*, **18**, 940; "Methods for Testing Stability of Explosives in Various Countries," *Z. ges. Schiess- und Sprengstoffwesen*, **5**, 21, 72, 210.

Finzi, "Ignition Points of Nitrocellulose and Smokeless Powders," *Gazz. Chim. Ital.*, **39**, 1, 549.

Jacqué, "German Railway Administration: Tests and Regulations of the," *Z. ges. Schiess- u. Sprengstoffwesen*, **4**, 175; "Causes and Methods of Determining Decomposition of Nitrocellulose," *Z. ges. Schiess- u. Sprengstoffwesen*, **1**, 395.

Lunge and Biebie, "Contributions to the Knowledge of Nitrocellulose," *Z. angew. Chem.*, **14**, 543, 561.

Mittasch, "Stability of Nitrocellulose," *Z. angew. Chem.*, **16**, 16, 929.

Obermüller, "Mittel. aus dem Berliner Bezirks-verein, etc., Oct., 1904," *See Wilcox, J. Am. Chem. Soc.*, **30**, 271.

Patterson, "Stability Tests of Smokeless Powder," *7th Intern. Congr. Appl. Chem., Explosives*, p. 99.

Pleus, "Some Improvements in the Apparatus for the Obermüller Manometer Test," *Z. ges. Schiess- u. Sprengstoffwesen*, **5**, 121.

Robertson, "On the Will Test for Nitrocellulose," *J. Soc. Chem. Ind.*, **21**, 819.

Rubin, "Testing Regulations and Black Powder Safety Explosive in England," *Z. ges. Schiess- u. Sprengstoffwesen*, **4**, 21.

Saposhnikov, "Rate of Decomposition of Nitrocellulose and Temperature," *J. Russ. Phys. Chem. Soc.*, **38**, 1186.

Snelling and Storm, "Behavior of Nitroglycerine when Heated," *Bureau of Mines, Technical Paper*, **12**, 1912.

Sy, "Stability of Nitrocellulose," *J. Am. Chem. Soc.*, **25**, 549, *Z. angew. Chem.*, **18**, 1824.

Wilcox, "Decomposition Curves of Nitrocellulose," *J. Am. Chem. Soc.*, **30**, 271.

Will, "Stability of Nitrocellulose," *J. Soc. Chem. Ind.*, **20**, 602; "Stability of Celluloid," *Z. angew. Chem.*, **19**, 1386.

Zschokke, "Testing of Explosives," *Z. ges. Schiess- u. Sprengstoffwesen*, **6**, 241.

¹ *J. Chem. Soc.*, **1901**, A, ii, 119.

² *Archiv. für Hygiene*, **1892**, 10.

³ *J. Chem. Soc.*, **1890**, A, 78.

⁴ Denigès, *Compt. rend.*, **1892**, 350.

⁵ Paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912. Published by permission of the Director of the Bureau of Standards.

as well as into the ordinary high temperature explosion test. In the former the time will vary with the heat insulation, in the latter the explosion temperature will vary with the rate of heating.

The apparatus used for the test is shown in Fig. 1. The heating bath consists of a crucible of iron or nickel, about 10 cm. in diameter and of approximately the same depth. The cover is of sheet metal about 3 mm. thick, with a flange that fits snugly into the crucible and projects slightly beyond the rim. One hole through the center of the cover is just large enough to permit the thermometer to pass. Symmetrically distributed around the center of the plate are 8 openings 15 mm. in diameter. The heavy metal supporting tubes are about 4 cm. in length and about 12 mm. internal diameter. The lower end of the tube is flanged so that the tube rests securely on the cover. The test tubes are about 9 cm. long and must be of such diameter that they will just slip freely into the supporting tube. A number of extra caps are provided to cover openings not intended to be used during the test. The heating liquid may be either paraffine, glycerine, or similar inert liquid which may be heated to 200° without boiling or fuming strongly.¹

The test tubes should dip about 4 or 5 cm. into the heated liquid so that their ends will be at about the center of the heated mass and may readily be removed

one at a time and replaced by fresh ones. For each explosion a clean tube should be taken.

The thermometer is supported by a metal clip which rests on the cover, the bulb being on a level with the lower ends of the test tubes. The thermometer used was standardized. Since the mercury thread projected but little above the highly heated zone the stem correction was found to be negligible. This should be checked with each apparatus and thermometer, for the various temperatures, when the apparatus is put together.

The heating bath is suspended in a conical piece of sheet metal wrapped with asbestos. The metal shield is cut so that the crucible will hang securely in the upper

small opening, while its larger end rests in the flanged tripod rim. With this apparatus and a small gas flame it has been easily possible to maintain the temperature constant for 15 or 20 minutes within half a degree. It is most convenient to have the burner set so that there is a tendency for the temperature to fall and to use a small accessory flame momentarily whenever necessary. With a temperature regulator or with electrical heating the ease of manipulation might, no doubt, be increased, but this is a matter of detail.

One or two stop watches¹ complete the equipment. When the apparatus has attained equilibrium at the desired temperature one or more of the test tubes is loaded by dropping in the sample of powder, the stop watch is started and a cork is dipped into the mouth of the test tube. The time until the explosion takes place is then noted.

The grains of the six-pounder smokeless powder are of convenient size to use directly. Powders of large caliber should be cut into pieces weighing about 0.2 gram each. Each sample of powder was tested at four temperatures, 160°, 170°, 180° and 200°. For the present purpose at least three tests were made at each temperature interval and curve was drawn through the average values.

The following series on powder A shows how closely duplicates may be expected to agree:

							Max. variations
							Av. Per cent
200°	1' 44"	1' 48"	1' 44"	1' 48"	1' 45"	1' 46"	2
180°	2' 55"	3' 06"	3' 10"	3' 04"	5
170°	4' 17"	4' 30"	4' 28"	4' 25"	3
160°	14' 20"	17' 40"	17' 34"	16' 36"	14

In general, the discrepancies appear to be greater at the lower temperatures. This is to be expected since the curves given further on show to what extent the influence of small temperature variations is magnified in the region of 160°. Furthermore, the irregularities are more pronounced in the "poor" powders.

The following set shows what can be expected as to reproducibility of the complete curve. The sample used was L and the second test was made one month later than the first. The averages only are given.

	200°	180°	170°	160°
I.....	1' 31"	2' 18"	3' 39"	7' 11"
II.....	1-27"	2' 31"	3' 43"	7' 30"

The following table and Fig. 2 give the results obtained with ten samples of smokeless and two samples of nitrocellulose. The samples were obtained through the Navy Department and I am indebted to the courtesy of G. W. Patterson, Powder Expert at Indian Head, for the selection of three classes: good, fair, and poor; and for the description of these samples, which I quote for comparison with the explosion periods:

Nitrocellulose A. "Specially prepared. Heat test, potassium-iodide starch, at 65.5° C., 4 min.; German test at 135° C.; 9 min. for litmus red."

Nitrocellulose B. "Heat test, potassium-iodide starch at 65.5° C., 42 min.; German test at 135° C., 38 min. for litmus red."

Powder Sample A. "Six-pounder. Diphenylamine as stabilizer. German test at 135° C.; litmus red, 2 hrs. 35 min.; explosion, 5 hrs. plus. Surveillance test at 80° C., 87 days; at 65.5° C., 307 days."

¹ The type of stop watch with two second hands, which may be stopped independently, has been found to be the most convenient form. With two of these, at least four samples may be observed simultaneously.

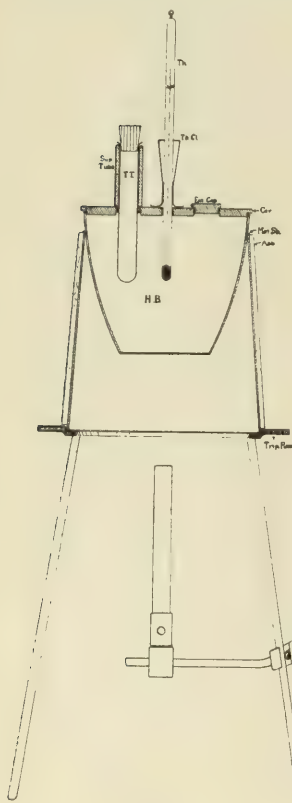


FIG. 1

¹ This form of apparatus has been devised by C. E. Waters in connection with work on lubricating oils.

Sample B. "Medium caliber. Diphenylamine as stabilizer. German test at 135° C.; litmus red, 2 hrs. 17 min.; explosion, 5 hrs. plus. Surveillance test at 65.5° C., 271 days."

Sample C. "Large caliber. Diphenylamine as stabilizer. German test at 135° C.; litmus red, 1 hr. 25 min.; explosion, 5 hrs. plus. Surveillance test at 65.5° C., 245 days plus."

Sample D. "Large caliber. No stabilizer. Rosaniline as indicator. German test at 135° C.; litmus red, 2 hrs.; explosion, 5 hrs. plus. Surveillance test at 65.5° C., 60 days."

Sample E. "Medium caliber. No stabilizer. Rosaniline as indicator. German test at 135° C.; litmus red, 1 hr. 35 min.; explosion, 5 hrs. plus. Surveillance test at 65.6° C., 74 days."

Sample F. "Six-pounder. Contains rosaniline and diphenylamine. German test at 135° C.; litmus red, 2 hrs. 25 min.; explosion, 5 hrs. plus. Surveillance test at 65.5° C., 375 days; at 80° C., 64 days."

Sample H. "Manufactured in 1901. When last tested it gave German test at 135° C.; explosion, 41 min. Surveillance test at 65.5° C. (1907), 79 days."

Sample I. "Manufactured about 1901. When last tested it gave German test at 135° C.; explosion, 33 min. Surveillance test at 65.5° C., 82 days."

Samples K and L. "These are both in very poor condition, giving only one day surveillance test."

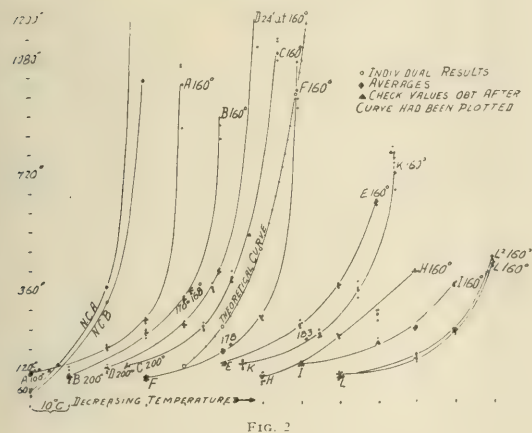


FIG. 2

The explosion periods obtained on these samples are shown in the accompanying table. The value underscored is the average value.

The curves embodying these results are given in Fig. 2. The curve marked "theoretical curve" is obtained on the assumption that the reaction velocity doubles for every 10° C. While the curves obtained from the explosion periods are of the same general type, it is apparent that the relation is not so simple as that shown by the "theoretical curve." What influence the stabilizer has upon the direction of the curves it is difficult to say with the data at hand. It does not follow that the stabilizer will affect the explosion test in the same manner as it does the heat test or the surveillance test. The stabilizer, while it removes the products of decomposition, may, of itself, act as a positive or negative catalyzer. If the decomposition be considered as the dissociation of an ester, the presence of a substance removing the products of decomposition will increase the rate. This has been noticed by Mittasch¹ for nitrocellulose with various basic additions and has been confirmed by myself in the case of pyroxyline plastics containing zinc oxide.

¹ Loc. cit.

	Nitro-cellulose	200° C.	180° C.	EXPLOSION PERIODS	
				170° C. over 30'	160° C. over 30'
A		33"	3' 20"		
		58"	6' 11"		
		37"	6' 56"		
		43"	6' 19"		
B		33"	4' 06"	16'	over 30'
		42"	5' 55"	17' 30"	
		34"	6' 06"	16' 45"	
		36"	5' 22"		
Powder A		1' 44"	1' 45"	4' 30'	14' 20"
		1' 48"	1' 46"	4' 17"	17' 40"
		1' 44"	3' 10"	4' 28"	17' 34"
		1' 48"	3' 04"	4' 25"	16' 36"
B		1' 54"	1' 41"	3' 37"	5' 23"
		1' 15"	1' 37"	3' 34"	5' 26"
		1' 65"	1' 27"	3' 44"	5' 36"
		1' 32"	1' 25"	5' 28"	5' 57"
C		1' 33"	1' 36"		14' 57"
				168°	
		2' 04"	4' 05"	6' 17"	17' 45"
		2' 04"	3' 15"	6' 28"	18' 25"
D		2' 10"	4' 50"	6' 55"	18' 18"
		2' 06"	4' 05"	6' 43"	18' 09"
			4' 20"	6' 15"	7' 00"
		1' 45"	2' 10"	4' 03"	5' 53"
E		1' 47"	2' 30"	4' 08"	5' 57"
		2'	2'	4' 10"	6'
		1' 58"			6' 56"
					28' 30"
F					24' 46"
				172°	171
		1' 35"	2' 10"	3' 55"	6' 10"
		2' 10"	2' 10"	4' 06"	5' 58"
H		2' 10"		4' 18"	6' 08"
		2' 05"		4' 06"	6' 05"
		1' 40"	1' 45"	2' 47"	3' 33"
		1' 41"	1' 38"	2' 45"	3' 23"
I		1' 48"	1' 43"	2' 49"	3' 31"
		1' 45"		2' 47"	3' 29"
		1' 15"	1' 38"	3' 32"	4' 45"
		1' 29"	1' 22"	3' 35"	4' 17"
K		1' 10"	1' 28"	3' 28"	4' 44"
		1' 15"		3' 32"	4' 35"
		2' 04"	2' 05"	3' 05"	3' 50"
		2' 10"	2' 05"	3' 05"	3' 49"
L		2' 02"	2' 04"	3' 20"	3' 56"
		2' 00"		3' 10"	3' 50"
		2' 05"	1' 50"	3' 29"	5' 55"
		2' 05"	1' 52"	3' 30"	5' 22"
L'		2' 14"	2' 04"	3' 50"	6' 15"
		2' 17"		3' 36"	5' 51"
		1' 31"	1' 30"	2' 13"	3' 38"
		1' 22"	1' 40"	2' 18"	3' 33"
L''		1' 27"	1' 31"	2' 22"	3' 47"
		1' 35"		2' 18"	3' 39"

K at 183°, 3' 29"; at 160°, 12' 43", 13' 20".

F at 178°, 3' 00", 3' 13".

A at 199°, 1' 47"; at 198°, 1' 53"; at 197°, 1' 52"; at 195°, 1' 56", at 193.5°, 2' 12".

That the curves do actually represent the stability of the powder with changing temperature and are not accidental is shown by the reproducibility of the various points along the curve, as shown in the table; by the fact that the curve having been determined by four points, determinations made at varying temperatures are found to fall on the curve; and by the fact that the complete curve can be reproduced at widely varying intervals. See curves L' and L''. The curves are undoubtedly characteristic for the sample. The deviations for individual points are not large enough to affect the general trend of the curve. What temperatures are chosen must probably be left to individual requirements; 190° would perhaps be pref-

cratic to see. At 150° we should have the apparent advantage that the differences between various samples become greater and the disadvantages that the test becomes slower and the results are more subject to accidental influences. The bend of the curve between 150° C. and 160° C. is, perhaps, its most characteristic portion.

The curves fall into three distinct groups for the samples tested, corresponding to their general classification of good, fair, and bad. The stable powders have a pronounced bend, while the ratio of explosion periods at 200° and 160° C. is at least 2 : 9. In the unstable samples this ratio falls as low as 2 : 3, and the points do not fit a smooth curve so well. The curves for the two samples of raw nitrocellulose are somewhat peculiar, being much flatter and corresponding more nearly to the theoretical curve.

The powders do not always fall in exactly the same order by this explosion test as they do by the surveillance or the heat tests, but it seems this is true to the same extent for the 135° German explosion test and the ones mentioned. This appears by comparison of the customary tests on samples D and H.

D: German test, 135°; litmus red, 2 hours; explosion, 5 hours; surveillance, 60. H: German test; explosion, 41 minutes; surveillance, 79.

From the results given it is evident that one explosion temperature, even if time is considered, does not give much information; while the determination of the characteristic curve does yield definite and specific information.

On account of the complexity of the conditions, the test can hardly be expected to tell all that is to be known, but I believe that with sufficient data it may even be made to throw some light on the actual effect of the stabilizer on the natural decomposition velocity of the powder, as distinguished from the length of time before the decomposition products become noticeable.

The proposed method gives more accurate determinations of the explosion temperature than the method of heating with rising temperature. It gives a better comparison of the relative stability of explosive substances. The test is, in effect, a determination of the rate of change of decomposition velocity with change of temperature and is, as such, characteristic for each sample.

BUREAU OF STANDARDS
WASHINGTON

KUKUI (CANDLE-NUT) OIL¹

By ALICE R. THOMPSON

Received May 5, 1913

Kukui oil, commonly known as candle nut oil, is extracted from the nut of the Kukui tree (*Aleurites triloba* or *A. moluccana*). The tree is generally distributed through Polynesia, Malaysia, Philippines, Society Islands, India, Java, Australia, Ceylon, Bengal, Assam, China, Tahiti, and Hawaii. In Hawaii, Kukui is found growing on all the islands in the lower mountain zone. As the oil is of considerable commercial value, investigations were made on the nuts and oil of samples sent to this station.

¹ Abstracted from *Press Bull.*, 39, Hawaii Experiment Station, U. S. Department of Agriculture.

The oil commonly known as candle nut oil belongs to the class of drying oils, valuable therefore as a paint and varnish oil. It is also used for soap-making and is a good illuminating oil. It is produced in large quantities in Australia, China, New Zealand and the Fiji Islands,¹ and is exported to America and Europe in ever-increasing shipments.

When extracted from the crushed kernel by ether or petroleum, the oil is light yellow in color, with a specific gravity of 0.92. When expressed, the oil may be dark colored due to impurities. It dries in thin films on standing several days.

At this station, a sample of oil was extracted by gasoline from the crushed kernels, the gasoline removed by evaporation and an analysis made on the oil to determine its chemical and physical properties. The values are as follows:

Specific gravity.....	0.92 at 15.5° C.
Saponification value.....	179.1
Iodine number.....	155.5
Holmer value.....	89.9
Soluble acids.....	1.71
Reichert-Meißl number.....	2.82

The fatty acids congealed to a pasty mass between 18° and 20° C. The oil itself was still fluid at -3° C. Fendler² found the congealing point of candle nut oil to be -15° C. The oil was soluble in ether and slightly soluble in alcohol. Concentrated sulfuric acid colored it dark brown.

The drying property of the oil is indicated by the high iodine value. Linseed oil, which is a fine drying oil, has an iodine value of 170-181.³

A sample of oil expressed from kukui nut was sent by Mr. Anderson to this laboratory. The oil was in a crude state, containing suspended matter, and had a dark red color. The oil had the following values:

Specific gravity.....	0.92 at 15.5° C.
Saponification value.....	190.2
Iodine number.....	164.2

In the following table are given the values found by chemists in the oil of *Aleurites moluccana* obtained in other parts of the world:

	(1)	(2)	(3)	(4)	(5)
Specific gravity at 15° C.	0.925	0.920-0.926	0.925	0.925	0.924
Acid value.....	1.72	0.97	0.5
Saponification value.....	204.2	184	-187.4	192.6	194.8
Iodine value.....	139.7	136.3	-139.3	163.7	114.2
Holmer value.....	96.4	95.5
Volatile acids.....	1.98	1.2
Titre.....	17.8
Butyro refractometer.....	76-75.5 (15° C.)	76 (25° C.)

(1) Imperial Institute, *Bull. Imp. Inst.*, 5, 135-136 (1907).

(2) De Negri, *J. Soc. Chem. Ind.*, 20, 909 (1901).

(3) Lewkowitsch, *Ibid.*, 20, 909 (1901).

(4) G. Fendler, *Ibid.*, 23, 613 (1904).

(5) Kassler, *Ibid.*, 22, 639 (1903).

The values vary to some extent in these analyses; nevertheless, the general characteristic of high iodine value and saponification extends throughout.

CONSTITUENTS OF THE KUKUI KERNEL

Several samples of nuts were obtained and the fat

¹ *Bull. Imp. Inst.*, 5, 135, 136 (1907).

² *J. Soc. Chem. Ind.*, 23, 613 (1904).

³ "Commercial Org. Analysis," Allen, Vol. II, Pt. 1, p. 97.

especially determined in the kernels. The fat content appears to vary but a few per cent in the kernels of nuts a year old or fresh. The fresh nuts naturally contain more moisture.

	1 year-old nuts	Fresh nuts	Immature nuts
	Per cent	Per cent	Per cent
Moisture.....	3.55	7.14	13.39
Fat.....	65.00	66.25	56.7
Ash.....	3.56	3.05	...
Protein.....	18.75	19.88	...
Fiber.....	2.14	1.39	...
Nitrogen-free extract by difference..	7.00	2.29	...
	100.00	100.00	

The fiber and the ash are very low, the principal constituents being fat and protein. It is of interest to note in this oil-seed the small percentage of hydrolyzable carbohydrates (only 1.40 per cent by analysis). A qualitative test showed the absence of starch in the kernels. The quantity of fat, if calculated to the water-free basis, is quite constant in the three samples.

Analyses made of the kernels of this same nut, *Aleurites moluccana*, by various chemists are given in the table below:

	(1) Per cent	(2) Per cent
Water.....	5.00	8.25
Oil.....	62.175	59.93
Protein.....	22.653	8.04
Nitrogen-free extract.....	6.827	17.62
Ash.....	3.345	3.56
Fiber.....	...	2.62
	100.00	100.00

(1) H. Semler, *Die Tropische Agrikultur*, 2, 515.

(2) N. S. Wales, *Agri. Gazette*, 17, 859 (1906).

The mineral constituents of the kernel were also determined in this laboratory, as shown in the following table:

	Per cent
Mn ₂ O ₄	0.03
CaO.....	0.17
MgO.....	0.60
P ₂ O ₅	1.59
K ₂ O.....	0.75

On extraction of the oil these constituents¹ increase in proportion to the dry matter. The residue contains, therefore, large amounts of phosphoric acid, potash and nitrogen, all valuable as fertilizing ingredients. Analysis of the residue of ground up kernels extracted with ether for two days is as follows:

	Per cent
Moisture.....	2.42
P ₂ O ₅	2.79
K ₂ O.....	2.77
Protein.....	53.75

Press cake obtained commercially by expressing the oil from kukui nuts would compare favorably with the residue, as most of the oil can be expressed. According to an article in the *Agricultural Gazette*,² 55 per cent oil can be obtained from kernels containing 60 per cent. Analyses of press cake made elsewhere shows it to be valuable as a fertilizer.

¹ Bull. Imp. Inst., loc. cit.

² Agr. Gaz. N. S. W., 17, 859 (1906).

ANALYSES OF PRESS CAKE

	(1) Per cent	(2) Per cent
Oil.....	8.8	5.5
Moisture.....	10.00	10.25
Ash.....	8.28	...
Protein.....	46.16	47.81
Fiber.....	1.47	...
P ₂ O ₅	4.39	3.68
K ₂ O.....	1.95	1.53
Mg and Ca.....	...	7.19

(1) Lewkowitsch, *J. Soc. Chem. Ind.*, 20, 909 (1901).

(2) H. Semler, *Die Tropische Agrik.*, 2, 515.

Press cake cannot be used as a fodder in spite of its apparent food value, as it has a poisonous effect upon stock.¹

The proportions of fat to kernel and whole nut were determined in several samples. In a sample one year old in which the fleshy husk that covers the shell when the nut is green, had decayed away, the kernel weighed 31.5 per cent of the hard nut. As the fat content of the kernel was 65 per cent, the fat content of the nut minus the husk, averaged about 20 per cent.

In a sample of fresh nuts, the kernel was 29.3 per cent of the nut minus the husk and 12.1 per cent of the nut with the husk on. The fat content of the kernel was about 66 per cent. It was, therefore, about 8 per cent of the nut with the husk, on and about 19.4 per cent of the hard nut minus the husk.

In another sample of fresh nuts, the kernel was 12 per cent of the nut with the husk on and 30.4 per cent of the hard nut minus the husk. The kernel contained about 57 per cent fat. The fat content of the whole, therefore, was about 7 per cent and of the nut minus the husk about 17 per cent.

HAWAII EXPERIMENT STATION
HONOLULU

THE DETERMINATION OF SODIUM BORATE IN SOAP²

By PAUL POETSCHKE

The customary method employed for the determination of borax in soap has been to extract the dry soap with 95 per cent alcohol, or, the soap without drying is extracted with absolute alcohol. The residue, insoluble in alcohol, is then treated with water and the borate determined by titration. It has been assumed that borax is insoluble in alcohol, undoubtedly, from the fact that this statement appears quite generally in the text-books.

About a year ago the author had occasion to conduct quantitative analyses of quite a number of commercial borax soaps and it was soon established that extraction with alcohol was unsatisfactory, owing to the solubility of borax in this liquid, even if the soap was thoroughly dried and extracted with absolute alcohol. When chemically pure sodium borate was boiled with absolute alcohol and carefully filtered until the filtrate was absolutely clear, it was found that the filtrate upon evaporation left a residue which readily dissolved in cold water, gave an alkaline reaction to methyl orange and a positive test for boron. The same

¹ *Agric. Gaz. N. S. W.*, 17, 889 (1906).

² Read before N. Y. Section, American Chemical Society, May 9, 1913.

sodium borate which had been thus boiled with alcohol was treated twice in the same manner and the individual filtrates evaporated to dryness. Both of these filtrates gave a residue which was readily soluble in cold water, the later solution giving an alkaline reaction to methyl orange and a positive test for boron. An alcoholic solution of boric acid left no residue on evaporation. This demonstrates conclusively that the material dissolved by the alcohol consisted of borax and that it could not have been due to free sodium hydroxide or free boric acid.

Two samples of commercial borax soaps were thoroughly dried at 100° C. and extracted with absolute alcohol in a Soxhlet extractor. The insoluble residue and the alcoholic extract were separately analyzed for the quantity of borax contained in each. Table I gives the results of these experiments, together with the total borax content of the soaps as determined by the method described in this paper.

TABLE I

Sample	Borax in alcohol extract Per cent	Borax in extracted residue Per cent	Total borax in extract and residue Per cent	Total borax content of soap Per cent
A.....	0.40	1.47	1.87	1.87
B.....	2.53	8.18	10.71	10.88

It is seen from the data in Table I that the error resulting from the solubility of the borax in alcohol amounts to 21.4 per cent of the total borax content in A, and 23.2 per cent in B, and that the borax found in the residue and extract agrees well with the total borax content of the soap.

An attempt was made to determine the borax by ignition of the soap with alkali carbonates. The ash was dissolved in water, slightly acidified with hydrochloric acid and boiled under a reflux condenser in order to expel carbon dioxide. After neutralizing the excess of acid with sodium hydroxide, using methyl orange as an indicator, the boric acid was titrated with *N*/10 alkali in the presence of glycerine, using phenolphthalein as indicator. Owing to the presence of silica in the soaps, this method failed to yield satisfactory results.

Wherry¹ has described a volumetric method for the determination of boric acid in insoluble silicates and an adaptation of this method was found to yield satisfactory results. It was found that silica was not always present in the soaps in sufficient quantity to give a satisfactory precipitation, so that it became necessary to add a fixed quantity of silica to the alkali carbonate used in the fusion mixture. The method as finally developed is as follows:

Weigh 10 grams of the soap (or 5 grams if more than 5 per cent of borax is present) into a platinum dish and add 2.15 grams of fusion mixture (consisting of 200 grams sodium carbonate, 15 grams silica in fine powder). To this mixture add 15 cc. of alcohol, mix with the aid of a glass rod and after washing the rod with a little alcohol, evaporate the mass to dryness on the water bath. Ignite until the combustible material is destroyed, cover the dish with a piece

of platinum foil and fuse. Completely disintegrate the fusion by boiling with water and transfer the solution to a 250 cc. round-bottomed flask. Acidify with 20 cc. of dilute hydrochloric acid (1:1), heat nearly to boiling and add a moderate excess of dry precipitated calcium carbonate. Connect with a reflux condenser and boil vigorously for 10 minutes. Filter out the precipitate through a folded filter, washing several times with hot water, but keeping the total volume of liquid below 100 cc.

Return the filtrate to the flask; add a pinch of calcium carbonate and again boil under a reflux condenser. Remove the flame and connect the top of the condenser with a water pump. Apply the suction until the boiling has nearly ceased. Cool to ordinary temperature, add 50 cc. of neutral glycerine and titrate the solution with 0.1 normal sodium hydroxide, free from carbonate, using phenolphthalein as indicator. After the end point is reached add 10 cc. more of glycerine and again titrate. Repeat this process until the addition of glycerine causes no further action on the end point. The number of cubic centimeters required multiplied by 0.00955 will give the equivalent of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) present in the solution.

A number of analyses were made in which a definite amount of chemically pure borax was added to castile soap which was free from borax. The results of these determinations are given in Table II:

TABLE II

Per cent sodium borate added	Per cent sodium borate found	
	A	B
10	10.00	9.99
7	6.96	6.96
5	4.91	4.96
3	2.95	2.96
2	1.97	1.96
1	0.95	0.98

It is evident from the table that the method gives results which are in close agreement with the actual borax content of the soap.

It is always advisable to test a soap qualitatively for borax before undertaking the quantitative determination. This is accomplished by placing one gram of the soap in a test tube, together with 10 cubic centimeters of dilute hydrochloric acid. The mixture is then heated to boiling which causes the fatty acids to rise to the surface. After cooling the tube under a tap of running water, the acid liquid is filtered through a wetted filter. A strip of turmeric paper is immersed in the filtered liquid and dried, when it will acquire a deep red color, which changes to green or blue on the addition of ammonia, if borax is present. A number of tests conducted with known amounts of borax show that the test performed in this manner is sensitive to 0.05 per cent of borax in the soap.

There is a considerable variation in the borax content of commercial borax soaps. Analyses of fourteen different brands are given in Table III.

It is thus apparent that a considerable number of the commercial borax soaps contain absolutely no borax, or practically none, whereas those which con-

¹ "Determination of Boric Acid in Insoluble Silicates," E. T. Wherry and W. H. Chapin, *J. Am. Chem. Soc.*, **30**, 1687.

TABLE III

Laboratory number	Per cent of borax
79188 Borated skin soap.....	None
79189 Antiseptic toilet soap, borated.....	1.96
79190 Best borax soap.....	None
79191 Borax soap.....	0.17
79192 Finest quality borax soap.....	0.10
79193 Borax soap.....	1.85
79194 Real borax soap.....	10.88
79195 White borax soap.....	6.44
79196 Refined borax soap.....	1.35
79518 Best borax soap.....	0.03
79519 Best borax soap.....	None
79520 Borax soap.....	3.42
79521 Borax soap.....	None
79522 Borax soap powder.....	None
82369 Borax soap.....	None
82570 Cocoa borax soap.....	None
82571 Borax washing compound.....	None

tain borax vary from 1.35 to 10.88 per cent.

In conclusion, I wish to acknowledge my indebtedness to my assistants, Messrs. J. A. Flanagan, M. J. Vinick and E. C. Pailer, for their assistance in the analytical work.

LEDERLE LABORATORIES
39 WEST 38TH STREET
NEW YORK CITY

DETERMINATION OF PHOSPHORUS IN STEELS CONTAINING VANADIUM

By J. R. CAIN AND F. H. TUCKER

Received May 19, 1913

It is known that vanadic acid, even when present in small quantity, interferes with the precipitation of phosphorus as phosphomolybdate. Where the quantity of phosphorus is small relatively to the vanadium, as in steel, the vanadium not only contaminates the precipitate which is obtained, but also retards the rate at which it is formed and may prevent complete precipitation.

While developing a method in this laboratory for the determination of vanadium by co-precipitation with phosphomolybdate,¹ it was observed that the vanadium is precipitated in this manner only when present in the quinquivalent condition; quadrivalent vanadium was not precipitated, neither was pervanadic acid. In some experiments made by adding enough hydrogen peroxide to a solution containing vanadium to convert all of it to the pervanadate, not the slightest co-precipitation was observed with large or small amounts of added phosphate. The precipitates of phosphomolybdate obtained had the normal canary-yellow color, in contrast to the orange-red tint of precipitates containing vanadium. Other tests also showed no vanadium in such precipitates.

These observations suggested the possibility of determining phosphorus in the presence of vanadium by converting the latter to pervanadic acid before adding the molybdate reagent. To test this question, determinations of phosphorus in the B. S. Vanadium Standard (No. 24), in the B. S. Chrome-Vanadium Standard (No. 30), and in some synthetic solutions containing varying proportions of iron, chromium and vanadium, were carried out by the alkalimetric method, except that the vanadium was converted, be-

fore precipitation of the phosphorus, to pervanadic acid by means of hydrogen peroxide. While this method yielded satisfactory results with the majority of the large number of samples tested, there were occasional irregularities which we were not able to eliminate. In cases where the method failed, the precipitates were red, the results were low, and no further precipitate formed after a long period of time. In a series of determinations with a given sample faulty results occurred only occasionally. A great deal of work was done in trying to find the causes of these apparently accidental failures by varying the concentration, temperature, acidity, etc., of the solutions, but without success.

Apparently the trouble is due to a decomposition of the hydrogen peroxide and of the peroxidized vanadium before complete precipitation of the phosphorus takes place, and this decomposition is probably caused by the presence of one or more of the numerous catalyzers which decompose hydrogen peroxide. Owing to this fact and to the further objection that hydrogen peroxide also peroxidizes the molybdenum of the precipitant, thereby causing possible abnormalities in the action of the latter, it was decided to abandon this method for general work. It is quite possible, however, that correct results on a given sample may be obtained by making several determinations and eliminating from the average those which are evidently wrong when judged by the criteria above indicated.

Experiments which resulted in the discovery of a satisfactory method based on reduction of the vanadium to the quadrivalent condition were then begun. The fact that phosphorus may be quantitatively precipitated by the molybdc reagent when present with vanadium in this condition² has long been known. We have found that the difficulty in applying this principle to the analysis of steel arises from the fact that whereas original solution of the metal must be made in nitric acid, if the direct molybdate precipitation is to succeed, the presence of this acid complicates the reduction of the vanadium as the operation is ordinarily carried out. It has often been attempted to reduce vanadium to the quadrivalent state by means of ferrous iron, but the statements in textbooks referring to this method indicate, directly or indirectly, that success has not been attained. Thus, Johnson³ states, and gives results indicating, that such reduction, as carried out in his experiments, did not give correct results for phosphorus. Brearley and Ibbottsons⁴ give determinations on two samples of ferrovanadium containing large amounts of phosphorus, where the vanadium had been reduced under conditions specified by them.

Whether or not the phosphorus content which Brearley and Ibbottson reported was correct cannot be deduced from their statements, for this element was not determined by any other method known to give a correct result. It is equally impossible to decide from their experi-

¹ Treadwell, "Kurz. Lehrbuch der Analy. Chem.," pp. 227 and 228, 4th ed., Vol. II, 1907.

² "Chemical Analysis of Special Steels, etc.," pp. 22 and 23, 1909.

³ "The Analysis of Steel Works Materials," p. 166, 1902.

⁴ Cain and Hostetter, B. S. Tech. Paper No. 8; THIS JOURNAL, 4, 250 (1912).

ments whether the vanadium was completely reduced at the time of precipitation. If it was not completely reduced (causing low results for phosphorus), there would have been produced a corresponding amount of the orange-colored precipitate which always forms in the presence of vanadic acid, but this, when associated with the large amount of normal phosphomolybdate which they obtained (their samples contained 0.65 per cent and 1.35 per cent phosphorus, respectively), might easily have escaped their notice. From other statements made by Brearley and Ibbottson on this subject¹ it would appear that they believe the formation of an orange-colored precipitate has little significance in affecting phosphorus results, the deficiency in phosphorus precipitated in such cases being compensated by the positive error caused by the vanadium associated with the precipitate. In this connection it may be stated that our results show that formation of a red or orange-colored phosphomolybdate always indicates incomplete precipitation of the phosphorus.

Having confirmed, by a series of results, the fact that phosphorus is quantitatively precipitated as phosphomolybdate in the presence of quadrivalent vanadium alone, the disturbing factors operating when vanadic acid is reduced by ferrous iron in nitric acid solutions of steels as a preliminary to the determination of phosphorus were investigated.

Duplicate nitric acid solutions of steel containing added vanadic acid were reduced with excess of ferrous sulfate. To one of the pair there was added the usual proportion of ammonia used in a regular phosphorus determination, and, after cooling, the color of the solution was compared with the companion solution to which no ammonia had been added. Not only had the blue color of the first solution due to reduced vanadium disappeared, being replaced by the yellow tint of vanadic acid, but the treated solutions usually gave but a slight test for ferrous iron. It thus appears that quadrivalent vanadium is oxidized by the nitric acid when the solution is heated by adding the necessary amount of ammonia. The vanadic acid thus formed would have prevented complete precipitation of phosphorus; moreover, most of the excess of ferrous iron, which would have tended to keep the vanadium reduced, had disappeared.

Solutions of steel containing vanadium and phosphorus were then prepared for precipitation of the latter by reducing with ferrous sulfate under the proper conditions to insure an excess of the reducing agent being present at the time of adding the molybdic reagent. When precipitation was made at 35° to 45° C., the solutions usually gave no test for ferrous iron after completion of the five-minute period of shaking generally recommended. When the reducing agent had thus disappeared, the oxidation of the hypovanadic acid was indicated by change in color of the solution, by abnormal color of the precipitate, and by low results. However, if precipitation was made at 15° C., excess of ferrous iron was almost always present.

¹ Loc. cit., p. 165.

We sought to determine whether phosphorus may be quantitatively precipitated as phosphomolybdate at low temperatures. With prolonged and thorough shaking or agitation of the solution, quantitative precipitation can be made at temperatures of 15° to 20° C., and our successful determinations, given in Table I, have been made at these temperatures. A 10-minute shaking suffices; the precipitate thus formed settles rapidly and filters as readily as that formed at 35° to 45° C., as in the ordinary procedure for determining phosphorus in steels.

Even with an excess of ferrous iron, as indicated by the ferricyanide drop test, red or orange-colored precipitates and low results were often obtained. The solutions in such cases had a deep red color. There was a strong odor of oxides of nitrogen and sometimes even evolution of these gases. It was evident, then, that under certain conditions vanadic acid in nitric acid solution would not be completely reduced by ferrous iron, even with a considerable excess of the latter present. The trouble was found to be caused by the presence of oxides of nitrogen, due to interaction of ferrous iron and nitric acid; for when the gases were expelled from the solution, for instance by passing carbon dioxide in the cold for a sufficient time, the deep red color disappeared, the phosphorus precipitates were normal in color, and the results were quantitatively correct. To further test this point, a vanadate solution was reduced by sulfurous acid, the excess of reducer removed, and the vanadyl solution thus formed added to the nitric acid solution of a vanadium-free steel. Oxides of nitrogen, formed during the solution of zinc in nitric acid, were passed into the solution thus prepared. A gradual disappearance of the blue color, due to reduced vanadium, was observed, and the phosphomolybdate precipitate obtained from the solution of the steel was orange-colored, both results indicating that the oxides of nitrogen had caused oxidation of the vanadium. Some experiments were also made by precipitating phosphorus from steels containing vanadium, by reducing the latter with an excess of ferrous sulfate, the flask in which precipitation was made being filled with carbon dioxide; under these conditions there was complete precipitation and the phosphomolybdate had the normal color. It thus appears probable that the nitric oxide (NO) formed by action of the ferrous salt in nitric acid serves as a carrier of atmospheric oxygen to the vanadyl compound.

The method of preparing solutions of steels for phosphorus determination in the experiments described above was the usual one of dissolving in nitric acid of 1.135 specific gravity, oxidizing with excess of permanganate solution, and destroying the excess of oxidizer (with simultaneous partial or complete reduction of the chromic and vanadic acids in solution) by ferrous sulfate, sulfurous acid, or a sulfite. After the observations above noted had been made, it was finally found that, observing the precautions shown to be necessary by the preceding experiments, samples in which the preliminary reductions of excess of permanganate, manganese dioxide,

etc., were made with ferrous sulfate almost always gave trouble through incomplete precipitation, red or orange-colored precipitates, etc., whereas, on the other hand, samples in which this reduction was made by sulfurous acid or a sulfite nearly always gave good results. In the latter class of samples, also, after addition of ferrous sulfate to complete the reduction of the vanadium before adding the molybdate reagent, no odor of nitrous fumes was noticeable. Experiments were then made with the idea of reducing the vanadium by sulfurous acid alone, without the use of ferrous salt at all. This can be done; the essential conditions are to keep the temperature of the solution low and to allow time enough. Phosphomolybdate precipitated from such solutions has the normal color, and precipitation is quantitative. On account of the long time necessary, however, reduction by sulfurous acid alone is not to be recommended for routine work.

Our conclusion, then, is that the presence of small amounts of sulfurous acid in the solutions where that reagent was used as a reducing agent for destroying permanganate, etc., counteracted the effect of, or prevented the formation of, oxides of nitrogen upon adding ferrous salt. The formation of these oxides being thus avoided, their effect in preventing complete reduction of vanadic acid by ferrous salt was eliminated, and hence correct results could be obtained for phosphorus.

As a result of these investigations, then, the following four conditions should be observed in precipitating phosphomolybdate in nitric acid solutions of steels containing vanadium by the method of reduction of the vanadium to the quadrivalent state:

(1) The temperature of precipitation should be held at a point (15° to 20°) where the nitric acid does not oxidize the excess of ferrous salt or the reduced vanadium before complete precipitation of phosphorus takes place; (2) the partial neutralization with ammonia, frequently used when phosphorus is precipitated as phosphomolybdate, must be made before reduction of the vanadic acid, otherwise the heat of neutralization causes reoxidation of most of the ferrous iron and reduced vanadium by the nitric acid; (3) care must be taken to prevent the action of oxides of nitrogen, formed by interaction of ferrous salt and nitric acid, on the reduced vanadium; since these substances seem to catalyze the oxidation of the vanadyl salt and may in some cases completely prevent precipitation of the phosphorus, owing to the large amount of vanadic acid so produced; (4) efficient means for shaking or agitation of the solutions in which precipitation is to take place must be provided. A fifth condition, not likely, however, to give trouble with ordinary care, is the avoidance of too great an excess of ferrous salt. Under certain conditions, not fully investigated by us, a large excess of ferrous iron in the presence of vanadic and molybdic acids causes reduction of the latter, which, of course, is to be avoided for the present purpose. When all these conditions are observed there is no co-precipitation of vanadium

in solutions containing as high as 1.5 per cent of this element. This point was verified by testing phosphomolybdate precipitates (from a steel containing 0.112 per cent phosphorus and 1.5 per cent vanadium) for vanadium by dissolving the precipitates in concentrated sulfuric acid, adding a drop or two of nitric acid and heating till fumes were given off strongly; on cooling, no yellow color developed, showing that no vanadium had been coprecipitated.¹

TABLE I

	Vanadium present, per cent approximately	Chromium present per cent approximately	Phosphorus present, per cent (certificate value)	Phosphorus found with—		Differences (in percentages on steel) with—	
				V present	V + Cr present	V present	V + Cr present
B. S. steel standards							
V steel No. 29..	0.15(a) ..	0.035	0.037	..	+0.002
	0.15(a) ..	0.038	+0.003
Cr V steel No. 30	0.21(a) 1.35(a)	0.043	..	0.046	..	+0.003	..
	0.21(a) 1.35(a)	..	0.048	+0.005	..
B. O. H. 0.2 C	0.2	0.5	0.0082	0.007	0.008	-0.001	-0.000
Renewal 11a..	0.4	1.0	..	0.008	0.007	-0.000	-0.001
	0.6	2.0	..	0.008	0.006	-0.000	-0.002
	0.8	3.0	..	0.008	0.010	-0.000	+0.002
	1.0	4.0	..	0.007	0.008	-0.001	-0.000
B. O. H. 0.8 C	0.2	0.5	0.2460	0.024	0.023	-0.001	-0.002
Renewal 14a	0.4	1.0	..	0.025	0.022	+0.000	-0.003
	0.6	2.0	..	0.024	0.024	-0.001	-0.001
	0.8	3.0	..	0.023	0.024	-0.002	-0.001
	1.0	4.0	..	0.023	0.022	-0.002	-0.003
B. O. H. 1.0 C	0.2	0.5	0.045	0.044	0.046	-0.001	+0.001
Renewal 16a..	0.4	1.0	..	0.046	0.047	+0.001	+0.002
	0.6	2.0	..	0.044	0.047	-0.001	+0.002
	0.8	3.0	..	0.046	0.050	+0.001	+0.005
	1.0	4.0	..	0.049	0.044	+0.004	-0.001
A. O. H. 0.2 C	0.2	0.5	0.084	0.087	0.085	+0.003	+0.001
Renewal 19a..	0.4	1.0	..	0.084	0.083	0.000	-0.001
	0.6	2.0	..	0.084	0.083	0.000	-0.001
	0.8	3.0	..	0.086	0.084	+0.002	0.000
	1.0	4.0	..	0.084	0.083	0.000	-0.001
B. O. H. 0.2 C	0.2	0.5	0.112	0.106	0.109	-0.006	-0.003
Renewal 9a..	0.4	1.0	..	0.111	0.117	-0.001	+0.005
	0.6	2.0	..	0.111	0.109	-0.001	-0.003
	0.8	3.0	..	0.110	0.116	-0.002	+0.004
	1.0	4.0	..	0.106	0.106	-0.006	-0.006

(a) Certificate values.

The method, which is described below, is adapted to any steel containing vanadium, no other element which ordinarily complicates the determination of phosphorus being present. If tungsten, titanium, arsenic, tin, etc., are present, their disturbing influence is eliminated by the usual methods for steels containing no vanadium. Nickel, copper, chromium, molybdenum, or aluminium, when present as alloying elements along with the vanadium, do not interfere. The details of the method are as follows: The solution of the steel, up to the point where precipitation of the phosphorus is to be made, is prepared as for an ordinary phosphorus determination by the alkali-metric method, *viz.*, solution of 1 to 2 grams in 100 cc. of nitric acid (specific gravity 1.135), oxidation with slight excess of permanganate solution while boiling, destruction of the excess of permanganate, etc., by a slight excess of sulfur dioxide or a sulfite, cooling of the solution and addition of 40 cc. of ammonia (specific gravity 0.96). Any steel which does not

¹ Cain and Hostetter, *loc. cit.*

give all its phosphorus to the solution by this method must be treated in an appropriate manner, so that the acidity, concentration of ammonium nitrate, and total volume obtained are always the same as by the method of solution directed. Slight deviations from these conditions are, however, probably without significance. Assuming solution of the steel and partial neutralization to have been made as directed, the solution is cooled to 15° to 20° C., 5 cc. of a saturated solution of ferrous sulfate and two to three drops of concentrated sulfurous acid are added. After addition of 40 cc. of molybdate reagent the solution is shaken in an efficient manner for 10 minutes. The precipitate, after settling (which is quite rapid), is then filtered off, washed in the usual manner, and titrated by the alkalimetric method.

The following table gives results by this method on synthetic solutions made with B. S. standard acid open-hearth, basic open-hearth, and Bessemer steels, of varying phosphorus and carbon content, to which vanadium was added as sodium vanadate and chromium as chromium nitrate. The acid and alkali solutions used for titrations were standardized against B. S. standard steels No. 19a (A. O. H. o. 2) and No. 9a (Bes. o. 2 renewal). The individual determinations in each series are single determinations only; the good agreement in all cases with the certificate values for phosphorus of the individual steels shows the reliability and accuracy of the method.

The time required is practically that for determining phosphorus in an ordinary steel.

BUREAU OF STANDARDS
WASHINGTON

A RAPID MODIFIED CHLORPLATINATE METHOD FOR THE ESTIMATION OF POTASSIUM¹

By W. B. HICKS

Received June 27, 1913

HISTORICAL

Many attempts have been made in recent years to develop a short practical modification of the chlorplatinate method for the estimation of potassium. These have proceeded along three essentially different lines, all of which have sought to avoid the necessity of estimating other constituents than potassium and sodium chlorides before undertaking the precipitation of the potassium. The first two modifications, the shortened method of Fresenius and the Lindo-Gladding method, are so well known that they need not be discussed here.

In the third modification the potassium solution is evaporated directly with chlorplatinic acid, the residue washed with alcohol, the potassium chlorplatinate reduced and either the chlorine titrated or the platinum weighed. Although such a procedure has been the subject of numerous investigations in Europe, it seems never to have found its way into American literature. Because of this fact, and the rapidity, reliability and practicability of this procedure, the author feels justified at this time in directing atten-

tion to this excellent method, and in presenting the results of experiments along this line.

Finkener,¹ in 1866, first used a reduction method for the estimation of potassium. He evaporated the potassium solution with chlorplatinic acid, washed the residue first with alcohol and then with ammonium chloride solution, reduced the K_2PtCl_6 by igniting in hydrogen, extracted the residue with water and weighed the KCl, obtaining excellent results in the presence of various other salts.

In 1873 Mohr² proposed to precipitate, wash and dry potassium chlorplatinate in the usual way, then to mix this precipitate with sodium oxalate, ignite, leach out with water, acidify with acetic acid and titrate the chlorine, using K_2CrO_4 as indicator.

De Koninck³ suggested, in 1881, to dissolve the potassium chlorplatinate in hot water, reduce with magnesium ribbon and titrate the chloride with silver nitrate solution. To avoid the formation of oxychlorides in the reduction with magnesium, Fabre⁴ suggested the addition of a drop of sulfuric acid which should be neutralized by means of $CaCO_3$ previous to the titration with $AgNO_3$. Diamant⁵ preferred to reduce the chlorplatinate solution with zinc dust rather than magnesium, because under the conditions no oxychlorides of zinc were formed. In a second investigation on the subject, De Koninck⁶ effected the reduction of the chlorplatinate by warming the solution with calcium formate. Stolba⁷ proposed, in 1884, to reduce the K_2PtCl_6 with amorphous silver. This reduction, according to Atterberg,⁸ proceeds too far and is not to be recommended.

Many reduction methods in which platinum is weighed have been proposed. Thus Hilgard⁹ reduced the K_2PtCl_6 by heating, while Meissl¹⁰ and Vogel and Haefcke¹¹ effected the reduction by heating the precipitate contained in a porous Gooch crucible in a current of hydrogen. Neubauer¹² substituted coal gas for hydrogen because it is more practical and gives equally good results. Sonstadt¹³ accomplished the reduction by heating the precipitate with mercury. In all cases after complete reduction the soluble salts were washed out and the platinum weighed.

In the wet way the oldest reduction method is that of Corenwinder and Contamine.¹⁴ According to their procedure, the K_2PtCl_6 dissolved in hot water is added to a boiling solution of sodium formate. This method is often slow and leaves adherent deposits on the walls of the vessel which are difficult to remove according to Jean and Trillat,¹⁵ who proposed to reduce

¹ *Pogg. Ann.*, **9**, 637 (1866).

² *Z. anal. Chem.*, **12**, 137 (1873).

³ *Rev. Univ. des Mines*, **9**, No. 2 (1881).

⁴ *Chem. Z.*, **20**, 502 (1896).

⁵ *Ibid.*, **22**, 99 (1898).

⁶ *Ibid.*, **19**, 901 (1895).

⁷ *Ibid.*, **8**, 456 (1884).

⁸ *Ibid.*, **22**, 538 (1898).

⁹ Hilgard, *Versuchstationen*, **42**, 174 (1893).

¹⁰ Meissl, *Ibid.*, **42**, 173 (1893).

¹¹ Landw. Vers.-Sta., **47**, 109 (1896).

¹² *Z. anal. Chem.*, **39**, 481 (1900).

¹³ *J. Chem. Soc.*, **67**, 984 (1895).

¹⁴ *Bull. de la Soc. Industrielle du Nord*, **1879**.

¹⁵ *Bull. de la Soc. Chim. de Paris*, [3] **7**, 228 (1892).

¹ Published by permission of the Director of the U. S. Geological Survey.

the chlorplatinate by adding a few drops of formaldehyde to the solution made alkaline with soda. This effects immediate reduction, the authors contend, and the platinum comes down in large flocks which are easy to wash. Warren¹ used formic acid and ammonia to effect the reduction.

In 1867 Roussin and Comaille² suggested the use of magnesium as a means of reduction in analytical chemistry, and later Scheibler³ used the metal in the analysis of gold and platinum salts of organic bases. In 1893 Villiers and Borg⁴ adopted this means of reducing the chlorplatinate in the estimation of potassium, in which they added fragments of magnesium ribbon to the solution slightly acidified with hydrochloric acid until reduction was complete. The platinum was then filtered off and weighed. Atterberg,⁵ in a series of investigations on the best means of reducing the chlorplatinate in which a large number of reducing agents were tried out, concluded that magnesium, mercury and thioacetic acid are best suited for this purpose. Thioacetic acid gives a voluminous precipitate of platinum and is therefore best used only with small amounts of platinum. Mercury gives good results only when in considerable excess and in hot, concentrated solutions. Magnesium, on the other hand, gives equally good results under all conditions and is therefore preferable. Later, this method of estimating potassium has been the subject of investigations by Regel,⁶ Grete⁷ and Fiechter.⁸

The question concerning what substances interfere with the determination of potassium by the proposed method is an important one. Vogel and Haefcke⁹ showed that sulfates do not interfere, while Neubauer¹⁰ obtained good results in the presence of sodium, calcium and magnesium chlorides and sulfates and large quantities of sulfuric acid. Atterberg¹¹ determined potassium in the presence of iron and alumina after the addition of citric acid. Earlier Villiers and Borg,¹² working on known samples, obtained 100 per cent of potassium in the presence of sodium phosphate, sodium and aluminum sulfates, and sodium, calcium, magnesium and iron chlorides. The present investigation has confirmed the results of these authors and has slightly extended the list of non-interfering substances. As a matter of fact, the writer has found no salts which seriously affect the estimation of potassium by this method and it is possible that aside from rubidium, caesium, ammonium and organic compounds, no substances do interfere with this determination.

METHOD

On the basis of the results in the literature cited

¹ *Chem. News*, **75**, 256.

² *Z. anal. Chem.*, **6**, 100 (1867).

³ *Deutsch. Chem. Gesell. Ber.*, **2**, 295 (1869).

⁴ *Compt. rend.*, **116**, 1524 (1893).

⁵ *Chem. Z.*, **22**, 522 (1898); **22**, 538 (1898).

⁶ *Ibid.*, **30**, 684 (1906).

⁷ *Ibid.*, **34**, 1040.

⁸ *Z. anal. Chem.*, **50**, 629 (1911).

⁹ *Landw. Vers. Sta.*, **47**, 109 (1896).

¹⁰ *Z. anal. Chem.*, **39**, 481 (1900).

¹¹ *Chem. Zeit.*, [2] **22**, 538 (1898).

¹² *Compt. rend.*, **116**, 1524 (1893).

above and of the outcome of experiments described below, the following procedure is recommended for the estimation of potassium. The method is applicable in the presence of chlorides, sulfates, phosphates, nitrates, carbonates, borates and silicates, salts of sodium, barium, calcium, strontium, magnesium, iron and aluminum, and is especially suited for the estimation of potassium in potassium salts, salines and mixed fertilizers in which only the quantity of potassium is desired, and also in organic fertilizers after an appropriate modification to remove ammonia and other organic bases which interfere with the determination.

The method follows: Prepare the solution in the usual way, acidify slightly with hydrochloric acid, add chlorplatinic acid solution slightly in excess of that necessary for the complete precipitation of the potassium present and evaporate the solution on the steam bath to a syrupy consistency, *i. e.*, until solidification occurs on cooling. Flood the cooled residue with a small quantity of alcohol of at least 80 per cent strength, grind thoroughly with a pestle made by enlarging the end of a glass rod, and allow to stand one-half hour. The alcoholic solution should be colored if an excess of chlorplatinic acid has been used. Pour the liquid through a small filter, using suction, and before adding more alcohol rub up the residue again with the pestle. Now continue the washing by decantation with small portions of alcohol until the wash liquid becomes colorless. Three or four washings usually suffice. Transfer the precipitate to the filter and wash two or three times with alcohol.

Dissolve the precipitate in hot water, washing it through the filter into a beaker of convenient size. To the hot solution add about 1 cc. of concentrated HCl and approximately 0.5 gram magnesium ribbon (which has been previously washed in water) for every 0.2 gram¹ potassium present, stirring the solution and holding the magnesium at the bottom of the beaker by means of a glass rod. When the magnesium has practically dissolved, add a few cubic centimeters of dilute hydrochloric acid and allow the flocculent platinum to settle. The supernatant liquid should be perfectly clear and limpid like water if reduction is complete. To make sure add more magnesium, in which case the solution will darken if reduction be incomplete. Now add concentrated hydrochloric acid and boil to dissolve any basic salts, filter, wash thoroughly with hot water, ignite and weigh. From the weight of platinum thus obtained calculate the per cent of potassium.

The writer carried out eight determinations in conjunction, filtering both the potassium chlorplatinate and platinum on paper, using a filter cone and suction pump, and finally igniting and weighing the platinum in porcelain crucibles.

EXPERIMENTAL PART

To determine whether or not the common associates of potassium interfere with its estimation by the proposed method, three series of experiments were carried out:

¹ Fiechter, *Z. anal. Chem.*, **50**, 632.

- (1) Blank determinations on a number of salt solutions.
- (2) Determination of potassium in known samples in the presence of various other substances.
- (3) Estimation of potassium in natural brines and salines with and without the removal of other constituents.

For this purpose the following solutions were prepared:

(1) Chlorplatinic acid solution containing one gram of platinum in 10 cc. of the solution.

(2) Potassium chloride solutions whose potassium content was carefully determined by repeated analysis.

(3) Solutions of the following salts: NaCl, Na₂SO₄, CaCl₂, BaCl₂, SrCl₂, MgCl₂, AlCl₃, Al₂(SO₄)₃, FeCl₃, Na₂HPO₄, Na₂B₄O₇, NaNO₃ and silicic acid.

Baker's analyzed chemicals were used for the preparation of these solutions with the exception of calcium, magnesium and aluminum salts, sodium sulfate and silicic acid, of which solutions were specially prepared to free them from potassium.

Blank determinations were made on each of these solutions by evaporating a definite quantity with chlorplatinic acid and proceeding according to the method described above for the estimation of potassium. In all cases no residue of K₂PtCl₆ could be seen, but on washing the filter paper with hot water and reducing the filtrate with magnesium a few flocks of platinum were noticeable in some cases. The results of these blank determinations are given in Table I:

TABLE I

No.	Substance taken	Weight taken Gram	Platinum solution used Cc.	Weight of platinum obtained Gram
1	NaCl.....	0.2	1.0	None
2	Na ₂ SO ₄	0.3	0.5	0.0003
3	CaCl ₂	{ 0.5 0.2	0.3 4.0	0.0002 0.0002
4	AlCl ₃	0.3	0.5	None
5	Al ₂ (SO ₄) ₃	0.3	0.5	None
6	FeCl ₃	0.5	2.0	None
7	Na ₂ B ₄ O ₇	0.3	0.5	None
8	SrCl ₂	0.3	0.5	None
9	BaCl ₂	0.3	0.5	0.0003
10	MgCl ₂	0.3	0.5	None
11	Na ₂ HPO ₄	0.4	0.5	0.0004
12	NaNO ₃	0.5	0.5	0.0003
13	Silicic acid.....	5.0 cc.	0.5	0.0006
14	{ Boric acid..... NaCl.....	{ 0.2 0.3 }	1.0	None

It will be observed that in no case is there more than a few tenths of a milligram of platinum. This trifling amount is to be attributed to small quantities of soluble chlorplatinates adhering to the filter paper or to traces of potassium in the salts themselves.

In the experiments on known samples the potassium chloride solutions used were first carefully analyzed with the results given below. The theoretical factors were employed in all cases in making the calculations:

No.	Sol. taken	KCl solution		KCl calculated from		Platinum found		KCl calculated from		KCl average Gram
		Cc.	K ₂ PtCl ₆ found Gram	K ₂ PtCl ₆ found Gram	Platinum found Gram	Platinum found Gram	Platinum found Gram	Platinum found Gram	Platinum found Gram	
1	{ 10 10	{ 0.6505 0.6514	{ 0.1995 0.1998	{ 0.2612 0.2616	{ 0.1995 0.1999	{ 0.1997		{ 0.2006 0.2004		{ 0.2005
2	{ 25 25	{	{	{	{					

Definite quantities of potassium chloride solution and of other salts were mixed, evaporated with chlorplatinic acid, and the method prescribed above was followed. The results are given in Table II:

TABLE II

No.	Salts added	Quantity of salts added Gram	KCl taken		Platinum found Gram	KCl calculated from platinum found Gram	KCl recovery Per cent
			Cc.	Gram			
1	NaCl.....	{ 0.2 0.2	{ 10 10	{ 0.1997 0.1997	{ 0.2617 0.2622	{ 0.1999 0.2003	{ 100.1 100.3
2	Na ₂ SO ₄	{ 0.2 0.2	{ 10 10	{ 0.1997 0.1997	{ 0.2624 0.2615	{ 0.2004 0.1998	{ 100.4 100.1
3	CaCl ₂	{ 0.2 0.2	{ 10 10	{ 0.1997 0.1977	{ 0.2628 0.2620	{ 0.2007 0.2001	{ 100.5 100.2
4	AlCl ₃	{ 0.2 0.2 0.3 0.3	{ 10 10 25 25	{ 0.1997 0.1997 0.2005 0.2005	{ 0.2607 0.2606 0.2623 0.2622	{ 0.1992 0.1991 0.2004 0.2003	{ 99.8 99.7 100.0 99.9
5	Al ₂ (SO ₄) ₃	{ 0.2 0.2	{ 10 10	{ 0.1997 0.1977	{ 0.2617 0.2613	{ 0.1999 0.1996	{ 100.1 100.0
6	FeCl ₃	{ 0.2 0.2	{ 10 10	{ 0.1997 0.1997	{ 0.2623 0.2626	{ 0.2004 0.2006	{ 100.4 100.5
7	Na ₂ B ₄ O ₇	{ 0.25 0.25	{ 25 25	{ 0.2005 0.2005	{ 0.2626 0.2627	{ 0.2006 0.2007	{ 100.0 100.1
8	SrCl ₂	{ 0.3 0.3	{ 25 25	{ 0.2005 0.2005	{ 0.2636 0.2631	{ 0.2014 0.2010	{ 100.4 100.2
9	BaCl ₂	{ 0.3 0.3	{ 25 25	{ 0.2005 0.2005	{ 0.2629 0.2626	{ 0.2008 0.2006	{ 100.2 100.0
10	MgCl ₂	{ 0.3 0.3	{ 25 25	{ 0.2005 0.2005	{ 0.2621 0.2612	{ 0.2002 0.1995	{ 99.9 99.5
11	Na ₂ HPO ₄	{ 0.4 0.4	{ 25 25	{ 0.2005 0.2005	{ 0.2611 0.2631	{ 0.1995 0.2010	{ 99.5 100.2
12	NaNO ₃	{ 0.3 0.3	{ 25 25	{ 0.2005 0.2005	{ 0.2637 0.2612	{ 0.2014 0.1995	{ 100.5 99.5
13	NaCl..... Na ₂ SO ₄	{ 0.3 0.5 }	{ 10 10	{ 0.1997 0.1997	{ 0.2608 0.2608	{ 0.1992 0.1992	{ 99.8
14	Silicic acid.....	{ 8.0 cc. 8.0 cc.	{ 25 25	{ 0.2005 0.2005	{ 0.2635 0.2635	{ 0.2011 0.2011	{ 100.3 100.3
15	Solution x(a).....	{ 0.5 0.5	{ 25 25	{ 0.2005 0.2005	{ 0.2618 0.2621	{ 0.2000 0.2002	{ 99.8 99.9

(a) Solution x represents a mixture of the following substances: H₂SO₄, NaCl, Na₂SO₄, CaCl₂, MgCl₂, FeCl₃, AlCl₃, Na₂B₄O₇ and Na₂HPO₄.

The figures indicate that the above-mentioned salts have practically no deleterious influence on the estimation of potassium, and that the method is sufficiently accurate for all commercial purposes.

In Table III are given the results of a few analyses obtained in checking up routine work:

TABLE III

No.	Character of sample	Total soluble		Plat- inum found Gram	KCl calculated Gram	KCl Percent
		Sample taken Grams	Present found Gram			
200	Earthy material.....	{ 2.000 2.000	{ 0.189 0.189	{ 0.0905 0.0318	{ 0.0247 0.0243	{ 1.24(a) 1.22
300	Earthy material.....	{ 2.000 2.000	{ 0.4320 0.4320	{ 0.1306 0.0505	{ 0.0401 0.0386	{ 2.00(a) 1.93
400	Earthy material.....	{ 2.000 2.000	{ 0.1303 0.1303	{ 0.1644 0.0670	{ 0.0506 0.0512	{ 2.53(a) 2.56
85	Brine.....	{ 10.47 10.47 10.47	{ 0.4782 0.4782 0.4782	{ 0.3123	{ 0.2398 0.2394 0.2386	{ 2.29 2.29 2.28
120	Brine.....	{ 10.81 2.70	{ 0.8765 0.2191	{ 0.0944	{ 0.2745 0.0721	{ 2.54 2.67(a)

(a) All constituents except Na, K and Mg chlorides previously removed.

These experiments were carried out in connection with the "Potash Investigation" in the U. S. Geo-

logical Survey, so that the results illustrate the agreement that should be obtained in practice.

The method recommends itself from the fact that it is well adapted for the carrying out of a number of determinations simultaneously, it is accurate, it is rapid in that most associates of potassium do not interfere, and it requires a minimum quantity of chloroplatinic acid solution.

U. S. GEOLOGICAL SURVEY
WASHINGTON, D. C.

THE CHEMICAL COMPOSITION OF COOKED VEGETABLE FOODS. PART III

By KATHARINE I. WILLIAMS.

Received April 14, 1913

The investigations described in the following pages are a continuation of the work published in the *Journal of the American Chemical Society*, Vol. XXVI, No. 3, March, 1904, and Vol. XXIX, No. 4, April, 1907. The main object of this work was to gain information regarding the composition of foods as served at table. A good deal has been published as to the composition of foods, but mainly dealing with the analysis of the raw materials. The fresh, green vegetables were bought when in full season: Borecole, also called Scotch Kale or Curly Greens, in February, Endive in March, Chicory in February, and the cereal foods purchased locally.

GENERAL PREPARATION OF THE SAMPLES USED

The first consideration was to obtain a sample of each food as it would be served at table, therefore, in the case of chicory, borecole, chestnuts, endive, and celeriac, the usual refuse in the way of stems, leaves and husks was removed before cooking; the percentage is shown in Table II.

With the cereal foods described there is no refuse or waste, either before or after cooking. The water used for cooking was that supplied by the Bristol Water Company, about 26° of hardness, chiefly due to calcium carbonate. No salt or sugar was added before or during the cooking process.

METHODS OF COOKING

Two classes of food are dealt with, viz.: (1) Those in which, on cooking in an excess of water which is finally drained off, loss of nutrients occur, and (2) those which absorb water during this process and which suffer no such loss.

Class I.—This class contains such vegetables as soya beans, green flagorets, and butter beans which, after soaking in water for 12 hours, were cooked slowly in boiling water until tender, the process being stopped when the skins commenced to crack. Celeriac was first pared and cut into thin slices, then cooked in boiling water for 30 minutes. Chicory, borecole and endive, after being washed, and the outer leaves and hard stems removed, were kept in boiling water until tender. In the case of chestnuts, the outer husk was removed, the skin taken off after placing in boiling water for 2 minutes, and the nuts then cooked until fit for use. Unpolished rice, after washing, was shaken into boiling water and cooked until quite tender.

Class II.—The various specimens analyzed in this

group were the following: Rice cooked by the method described in the U. S. Department of Agriculture, *Farmers' Bulletin*, No. 256, page 38. Boyd's banana food: in this case the directions on the tin were followed. Frame food, when the directions given by the Frame Food Co. were followed. Provost barley, prepared by Messrs. R. Robinson & Son, of Annan; 142 grams were added to 1,136 cc. boiling water, the whole kept boiling for 15 minutes. Provost barley and oats, both of which are partially cooked before coming into the market: one part of barley was added to six parts of oats and treated in a similar fashion to the previous. Plasmon arrowroot: 25.6 grams were made into a paste with 80 cc. of warm water, then 204 cc. more water added; the whole boiled for 2 minutes with continual stirring. Banana flour: 12.7 grams made into a paste with 50 cc. water, then cooked for 20 minutes with the addition of 100 cc. water. *Revalenta arabica*: when the directions on the tin were followed.

Asparagus belongs to neither class; it was already cooked, being a bottled sample of "Le Success" system. P. Phillips, *Asperge Argenteuil*. Each bottle contained eight heads of the vegetable; the average weight was 209 grams, the average volume of liquid 54 cc. per bottle.

LOSSES IN THE PROCESS OF COOKING VEGETABLES

To ascertain the loss of nutrients in the process of cooking, the liquid that was drained off from the weighed substance was evaporated over a water bath, the solid obtained finally dried in an air bath at a temperature not exceeding 110° C.; the dish was cooled in a desiccator, weighed, the residue reduced to a fine powder, again weighed, and replaced in the air bath until the weight was constant. From the data obtained the percentage of loss was calculated. Two determinations were made in every case.

Table I shows the total solids in uncooked vegetable foods, the percentage of that solid lost in cooking, the weight in grams, the percentage of protein and ash in the residue recovered from the liquid drained off from the cooked food; these percentages were determined by the methods described for the dry powder foods.

	Dry matter in raw food Grams	Loss in cooking Per-centage	Loss in cooking Grams	Percentages of loss	
				Protein	Ash
Rice.....	85.85	10.90	9.36	6.94	...
Celeriac.....	9.30	47.65	4.43	10.59	5.36
Butter beans.....	85.95	9.61	8.25	28.20	5.54
Green flagorets.....	85.46	8.53	7.29	26.16	17.05
Soya beans.....	86.85	9.22	8.01	...	13.39
Chestnuts.....	43.12	9.77	4.21	54.18	7.08
Chicory.....	4.95	18.25	0.90	42.50	12.05
Borecole.....	10.82	48.92	5.29	41.42	15.77
Endive.....	8.87	27.89	2.47	29.48	18.75

The liquid in which the asparagus had been preserved was found to contain 2.41 grams of solid on evaporation, 16.9 per cent of which was protein.

It will be seen celeriac contains only 9.3 grams of solid matter and the loss is 47.6 per cent or 4.4 in grams; borecole loses 48.9 per cent of solid matter; butter beans only lose 9.6; green flagorets, 8.5 per

cent, the percentage of protein in the material left after evaporation is highest in the case of chestnuts, chicory and borecole. With the rice boiled in an excess of water only 10.9 per cent or 9.36 grams of the solid is lost, 6.9 per cent of that being protein, but, as will be noted in the cooked rice, the dry powder contains only 6.84 per cent protein, and any loss of this nutrient should be avoided. The data of the loss in cooking is not complete; to get full results larger amounts of the various vegetables should be used; the original idea was merely to determine the percentage, and not the constituents of the residue, but further details are given as far as could be determined with small amounts available.

TABLE II

	Price per pound in pence, d	Refuse — leaves and stems — per cent	As purchased — Used for cooking, per cent	Weight before cooking—grams	Weight after cooking—grams	Percentage water in raw food	Percentage water in cooked food
Banana flour	6	100	1108.7	10.22	91.91
Soya beans	3½	100	222.8	13.15	66.14
Green flagorets	8	100	210.0	14.54	62.77
Plasmon arrowroot	18	100	1135.0	13.20	92.90
Frame food	12	100	1561.3	4.97	93.85
Provost barley	4	100	1009.1	4.32	90.53
Provost barley and oats	3	100	603.5	10.57	85.17
Asparagus	25	100	92.18
Boyd's banana food	21	100	774.4	9.62	88.33
Rice	3	100	271.9	14.15	71.88
Rice (cooked, Method II)	3	100	361.9	14.15	76.32
Celeriac	3	6.64	93.36	100	87.1	90.7	94.41
Butter beans	4	100	215.4	14.05	63.94
Chicory	8	11.23	88.77	100	73.2	95.05	94.59
Chestnuts	6	12.48	87.52	100	134.5	56.88	71.08
Borecole	1½	38.11	61.89	100	50.6	89.18	89.05
Endive	5	52.01	47.99	100	140.0	91.13	95.43
Revalenta arabica	38	100	1556.8	11.26	94.30

Every sample was weighed before and after cooking, as is shown in Table II. The prices per pound of the raw substance are given, and also, for the sake of comparison, the percentages of water in the raw and cooked conditions; the refuse before cooking and the edible portion of the green vegetables; in these cases the percentage of water in the raw vegetables is given only for those edible portions actually used in cooking.

This table shows the great increase in bulk which the cereal foods undergo, in consequence of the absorption of water in the process of cooking; thus 100 grams of plasmon arrowroot swell up and become 1,135. The legumes also increase greatly in weight, but in the case of chicory and borecole there is a decrease from 100 grams to 50.6 with the latter, with chicory to 73.2 grams; in the case of borecole the percentage of water is practically the same for the cooked and uncooked condition, but 27.9 per cent of solid matter was lost in the process of cooking. The refuse before cooking shows a very high percentage with borecole and endive. Comparing the two methods of cooking rice, it will be noticed in method I that after the excess of water has been drained off there is 272 times the original weight of the rice taken, cooked by method II 362 times its original weight, but in this case there is no loss, whereas by the former method the loss amounts to 9.36 per cent of solid matter.

ANALYSIS OF THE EDIBLE PORTION

Determination of Water. Full details of the method used will be found in a previous paper.¹

At least two estimations were made in every case. To understand the degree in which it is possible to reproduce the results, I may state that in the case of plasmon arrowroot, the first determination gave 92.88, the second 93.02, the third 92.88, giving a mean of 92.90. In the case of butter beans, the first determination gave 63.92, the second 63.96, the mean being 63.94. The powders were placed in well stoppered bottles and used for the other determinations.

Fat or ether extract, and ash or mineral matter were also determined by the methods previously used. Several determinations were made. In the case of frame food, the results were 4.42, 4.62, 4.49, giving a mean of 4.59 per cent for ash.

Woody Fiber.—The method used is one adopted by the American Association of Agricultural Chemists, and described in *Bull.* 107 (revised), p. 56, U. S. Department of Agriculture, Bureau of Chemistry. The strength of the solutions was determined by titration.

Nitrogen.—Gunning's method modified to include the nitrogen or nitrates, as described in "Food Inspection and Analysis" (page 63), by Albert E. Leach, was used in this series of determinations, when possibly four estimations were made.

Protein.—Was calculated by multiplying the nitrogen previously determined by the factor 6.25.

Sulfur and Phosphorus.—The methods used are fully described in the author's previous paper.

Starch.—This was determined by direct acid hydrolysis using Sachsse's method modified, as described in *Bull.* 107, p. 53. Between 2.5 and 3 grams of the dry powder were taken, placed in a small bottle with 50 cc. of water, and then in the shaking apparatus for one hour; this method was found to give a better result than stirring the mixture in a beaker. The contents of the bottle were well washed with 250 cc. of water. Then the insoluble residue was heated for 2½ hours with 200 cc. water and 20 cc. hydrochloric acid (sp. gr. 1.125), in a flask connected with a reflux condenser, then cooled and nearly neutralized with sodium hydroxide. The volume was made up to 250 cc., filtered and clarified with alumina. When necessary the solution was concentrated at 100° C., and finally filtered before titrating with Soxhlet's Modification of Fehling's solution. The determination was made by direct weighing of the cuprous oxide as directed in *Bull.* 107, p. 53. In a few cases the results were confirmed by the volumetric method, titration with Fehling's solution. The following data were obtained and from them the amount of starch present was calculated:

	Volumetric Per cent	Gravimetric Per cent
Provost barley and oats	{ 70.0	69.6
	{ 75.1	74.2
Provost barley	59.8	59.4

In soya beans, however, a qualitative examination with iodine gave negative results, conse-

quently the carbohydrate present was taken as glucose.

The work described was undertaken with the idea of arriving at a clearer knowledge of the composition of foods as served at table. It is difficult to compare the results obtained with those of other investigators, since most of the work published deals with uncooked foods, and even in the raw condition great differences in composition occur, and these are accentuated in the process of cooking. With cereal foods there is no loss of nutrient, but with vegetables of the type of celeriac and butter beans, some of the soluble matter is lost in cooking. Borecole shows a decrease in weight (100 grams before 50.6 after), while 48.9 per cent solid matter is removed during the process of cooking, but the actual percentage of water is practically the same; so this vegetable is an exception to the general rule that vegetables increase in weight. In a former paper¹ it is shown that Broccoli does not increase in weight, while asparagus is another exception—100 grams before weigh only 50.9 after cooking. The loss of weight is probably mainly due to the loss of soluble nitrogenous compounds. It may be noticed from Table IV how little real nutrient these foods contain; the percentage of water is lowest with butter beans, soya beans, and green flagorets; all three legumes absorb less water than dried peas, as before determined; but the percentage of fiber is highest with soya beans (3.08), and 2.88 per cent with green flagorets. Soya beans give the largest percentage of protein, 16.00, also of fat, 6.05 per cent.

TABLE III—COMPOSITION OF THE EDIBLE PORTION OF THE COOKED VEGETABLE FOODS

	Proximate analysis of the water substance						Ultimate analysis of the dried substance		
	Ash	Protein N \times 6.25	Fat other ex- tract	Woody fiber	Starch	Starch by difference	Nitrogen	Sulfur	Phosphorus
Banana flour....	3.78	28.46	0.74	2.07	62.25	64.95	4.55	0.18	0.01
Soya beans.....	3.62	47.26	17.87	9.1	22.62	22.14	7.52	0.63	0.55
Green flagorets..	2.48	33.80	2.36	7.75	56.87	52.61	5.40	0.13	0.12
Plasmon arrow- root.....	3.21	11.43	0.12	0.02	86.20	85.22	1.82	0.41	0.54
Frame food.....	4.59	11.73	13.46	1.35	74.30	68.87	1.88	0.68	0.55
Provost barley... and oats.....	1.42	30.41	0.41	0.95	69.88	66.81	4.86	0.21	0.11
Asparagus.....	1.87	18.11	2.81	2.06	74.37	75.15	2.88	0.18	0.35
Boyd's banana food.....	16.80	22.50	4.79	6.71	56.89	49.20	3.60	0.60	0.04
Rice.....	0.38	6.84	0.20	0.34	96.30	94.24	1.09	0.19	0.07
Rice (cooked, Method II) ..	0.39	7.50	0.24	0.40	90.07	91.47	1.20	0.21	0.02
Celeriac.....	7.57	17.12	2.73	16.11	50.45	56.47	2.74	0.33	0.33
Butter beans.....	3.37	24.86	2.29	7.44	59.62	62.04	3.98	0.24	0.34
Chicory.....	5.92	26.39	1.19	9.37	55.39	56.41	4.22	0.57	0.63
Chestnuts.....	2.22	12.45	2.79	5.35	81.18	77.19	1.99	0.42	0.18
Borecole.....	7.63	33.80	6.66	9.90	36.06	42.01	5.40	0.35	0.60
Endive.....	12.25	11.42	5.04	15.61	59.81	55.68	1.83	0.38	0.57
Revalenta ara- bica.....	2.63	21.04	0.53	1.18	76.90	74.62	3.38	0.35	0.32

Table III gives full details of the analysis of the dried powdered foods, showing the percentage of ash, protein (calculated from nitrogen), fat, woody fiber, starch by direct acid hydrolysis, and by difference. Ultimate analyses are also given for nitrogen, sulfur and phosphorus.

Table IV gives the proximate analysis calculated on the natural moist condition, in order to show clearly the true value of the foods under consideration.

TABLE IV—PROXIMATE ANALYSIS CALCULATED FOR THE MATERIALS IN THEIR NATURAL MOIST CONDITION

	Protein					Starch by differ- ence	
	Water	Ash	N \times 6.25	Fat	Fiber	Starch	ence
Banana flour.....	91.91	0.31	2.30	0.06	0.18	5.03	5.22
Soya beans.....	66.14	1.23	16.00	6.05	3.08	7.65	7.50
Green flagorets..	62.77	0.92	12.56	0.88	2.88	21.22	19.99
Plasmon arrowroot..	92.90	0.22	0.81	0.01	0.01	6.12	6.05
Provost barley.....	90.53	0.13	2.88	0.04	0.09	6.61	6.33
Provost barley and oats.....	85.17	0.27	2.68	0.42	0.30	11.02	11.16
Asparagus.....	92.18	1.31	1.76	0.37	0.52	4.44	3.88
Frame food.....	93.85	0.27	0.72	0.82	0.08	4.63	4.27
Boyd's banana food..	88.33	0.56	3.90	0.38	0.14	6.26	6.69
Rice.....	71.88	0.10	1.92	0.05	0.09	27.07	25.96
Rice (cooked, Method II) ..	76.32	0.07	1.77	0.06	0.09	21.32	21.69
Celeriac.....	94.41	0.42	0.95	0.15	0.90	2.82	3.17
Butter beans.....	63.94	1.21	8.96	0.82	2.68	21.67	22.39
Chicory.....	94.59	0.32	1.42	0.10	0.51	2.99	3.06
Chestnuts.....	71.08	0.64	3.59	0.81	1.54	23.46	22.34
Borecole.....	89.05	0.83	3.71	0.73	1.08	3.94	4.60
Endive.....	95.43	0.55	0.52	0.23	0.71	2.73	2.56
Revalenta arabica....	94.30	0.15	1.19	0.03	0.07	4.38	4.26

TABLE V

	Nutritive ratio		Heats of combustion calories calculated
	1	2	
Banana flour.....	1	2.2	306.1
Soya beans.....	1	1.53	1532.2
Green flagorets..	1	1.9	1467.0
Plasmon arrowroot.....	1	7.6	293.3
Frame food.....	1	9.0	295.5
Provost barley.....	1	2.3	292.8
Provost barley and oats.....	1	4.4	599.4
Asparagus.....	1	3.0	288.9
Rice.....	1	14.1	1192.0
Rice (cooked, Method II) ..	1	12.1	950.5
Celeriac.....	1	3.3	171.6
Boyd's banana food.....	1	1.8	449.4
Butter beans.....	1	2.6	1331.2
Chicory.....	1	2.2	190.1
Chestnuts.....	1	7.0	1181.0
Borecole.....	1	1.5	381.8
Endive.....	1	7.2	154.6
Revalenta arabica....	1	3.7	231.1

Table V is calculated from Table IV, and is added so that dietaries can be easily computed. All dietary standards must be based on the nutrients required by individual, or class, on the assumption that the body has to be supplied with sufficient protein to replace the nitrogenous substances consumed in the body, and enough energy to supply the demand for heat, muscular and other work. The chief function of carbohydrates and fat is to serve as fuel; it is more important that they should be in sufficient amount, rather than in definite relative proportion to one another.

The ratio between the amounts of other organic substances and protein is called the nutritive ratio. As the fuel value of fat is about two and one-third times that of protein or carbohydrates, the quantity of fat is multiplied by $2\frac{1}{3}$, and added onto the carbohydrates; the nutritive ratio is obtained by dividing this sum by the amount of protein. If the fats and carbohydrates are greatly in excess of the protein, the nutritive ratio will be wide, becoming narrower as the relative amount of protein increases. Pro-

¹ J. Am. Chem. Soc., 26, 247.

essor Atwater gave as the evidence obtained from the study of American dietaries

	Nutritive ratio
Woman with light muscular work	1 : 8.7
Man without muscular work	1 : 8.5
Woman with moderate muscular work	1 : 8.6
Man with moderate muscular work	1 : 8.8

In the third column of Table V, the heat of combustion is given in calories per kilogram. The values are calculated by the use of Rubner's factors: 4.1 calories for a gram of protein, the same for a gram of carbohydrate, and 9.3 for a gram of fat.

It will be observed that rice gives the widest nutritive ratio, 1 : 14.1, owing to the large amount of starch present; the same may be said of frame food, 1 : 9.0; soya beans, with 1 : 1.3, and green flagorets with 1 : 1.9, show the narrowest. Provost barley and oats, 1 : 4.4, is perhaps the most satisfactory ratio on the list.

THE UNIVERSITY
BRISTOL, ENGLAND

PEPPERMINT OIL INDUSTRY IN JAPAN

By YEINOSUKE SHINOSAKI

Received May 24, 1913

Nowadays the Japanese peppermint fields are chiefly located in Hokkaido, Okayama and Hiroshima

becoming the principal districts of the cultivation and the oil production in Japan; at least ninety per cent of the total production of the oil in Japan comes from the said districts.



1—KAMI-KAWA (ISHIKARI) 3—MONBETSU (KITAMI)
2—KAMI-KAWA (TESHIO) 4—TOKORA (KITAMI)

The first peppermint cultivation in Hokkaido was commenced at Kami-Kawa (in the province of Ishi-

TABLE I

Name of the district	Principal villages	Cultivated area Acres		Oil products Weight in lbs		Price in dollars		Number of producers		Number of laborers	
		1910	1911	1910	1911	1910	1911	1910	1911	1910	1911
Tokoro (Kitami)	Notsukeushi	2,588	3,244	88,000	73,128	132,000	164,538	1,074	1,089	1,998	1,989
Monbetsu (Kitami)	{ Kamiyubetsu Shimoyubetsu }	2,193	3,091	82,800	114,947	84,200	224,146	895	955	2,025	1,613
Abashiri (Kitami)	Mihoro	140	142	3,813	3,827	5,720	5,740	30	30	70	70
Kami-Kawa (Ishikari)	{ Aibetsu Nagayama }	1,135	1,676	35,323	34,567	46,608	64,425	172	221	660	698
Kami-Kawa (Teshio)	{ Shibetsu Kaminayoro }	287	450	9,200	15,307	13,775	64,502	68	162	302	601
All others							32,251				
Total		6,343	8,603	219,136	241,776	282,303	491,100	2,239	2,457	5,055	4,971

chiefly located in Hokkaido, Okayama and Hiroshima prefectures. Formerly Okayama and Hiroshima had

kari) by the immigrants from Yamagata prefecture. Now the most important center in this place is the province of Kitami, in which Notsuke-Ushi (Tokora) and Yubetsua (Monbetsu) are again the chief places of the production.

In 1910 and 1911 the total production in this place amounted to about 110 and 120 tons, the details of which are to be given presently in a tubular form.

The accompanying map illustrates the chief peppermint districts in Hokkaido.

CULTIVATION

There are two varieties of Japanese peppermint, *Mentha Arvensis*, known as the "Aomaru" and "Akamaru" mint. The former is noted for its vigorous propagation but is inferior in quality. The Japanese peppermint oil is, therefore, prepared from the Akamaru mint.

The stem of the Akamaru variety presents a violet-red color which disappears as the plant



PEPPERMINT FARM AT NOTSKEUSHI VILLAGE IN TOKORO (KITAMI)

controlled the market, but during nearly the last six years the industry in Hokkaido has superseded others,

grows. The petals of its flower are of light violet color. In Hokkaido the mint sprouts in the spring and blossoms in the autumn. It is generally cultivated in a district of warm and dry alluvial soil. Being a perennial plant, the mint contains the largest amount of oil two or three years after its original planting. After a certain period, however, the oil is gradually reduced. It is, therefore, transplanted in newly opened districts when the farms become four or five years old.

The quality of Japanese peppermint oil is inferior to that of German and English origin, chiefly on account of its bitter taste. To improve the quality, the peppermint of English and German origin was put on a trial cultivation at the Katami Branch of the Agricultural Experimental Station of Hokkaido a few years since.

CUTTING AND DRYING

Before frost sets in, the peppermint harvesting is carried on annually on a dry day in September, when it is in full bloom. The cuttings are tied up in bundles and then bound into a series of small sheaves with straw ropes. These are dried by hanging on shelves constructed upon the roofs of farm cottages or drying huts, especially built for the purpose. They require three or four weeks for complete drying. The harvest from one acre is about 2200-3300 lbs. of the dried herb.

DISTILLATION

The peppermint oil is prepared by the steam distillation of the dried herb, which is carried out by the farmers in the intervals of farming (from the middle

wooden vat with a small opening in the center of the bottom. The condenser is a cast iron kettle of inverted conical form. This apparatus is an old type of the kind and is especially employed by the immigrants from the Yamagata prefecture.

In carrying out the process, the boiler is filled with water and then hearth-fired. The wooden vat is placed over the kettle, filled with the dried herb, and



DRYING PEPPERMINT HERB AT NOTSUKESHU FARM

then covered with the condenser filled with water. The steam carries with it the oil, which condenses on the lower surface of the condenser; the mixture of water and oil passes through a rectangular wooden tube (sometimes bamboo split into two) into a receiver called a "Mizukiri-Kame." The capacity of the wooden vat is about 124-166 lbs. of the dried herb, from which a yield of oil amounting to about 1.07-1.6 per cent of the dried herbs is obtained.

(2) By the so-called "Kikaido" still (a wooden vat) and a spiral condenser. This type of still was generally employed at Okayama and Hiroshima prefectures in former days but rarely in Hokkaido. The form of the vat is the same as the above, but after charging, it is tied down by an iron chain fixed in the floor to tighten the joint between wooden vat and kettle so as to prevent as far as possible the escape of steam. Its capacity is about 207 lbs. of the dried herbs. On the upper part of it there is placed a metal pipe, which is connected to a spiral condenser (metal) in a wooden trough filled with water.

(3) By the so-called "Seiro" still (the wooden steaming box). It originated in Hokkaido and is generally employed there, especially in Kitami district. It consists of three or six sets of wooden frames which are superimposed. The same kind of connecting pipes and condenser referred to already is used. The space of the frame around the rim is packed by strips of moist cloth, rags, wheat flour or rice bran. The Seiro is placed as tightly as possible on a suitable



DISTILLING PEPPERMINT OIL BY HANGING VAT STILL AT NAGAHAMA VILLAGE IN THE DISTRICT OF KAMIKAWA (ISHIKARI)

of October to the last of November) in improvised plants close by the drying huts. The distillation of oil is carried out as follows:

(1) By means of a wooden vat-still and the so-called "Tensui-Kama" condenser. The still is the

cast iron kettle filled with water and held down tightly by means of a chain fixed to the ground. It can hold 400-500 lbs. of the dried herbs from which a 1.2-1.6 per cent yield of the oil is obtained.

The advantages of the "Seiro" are: the larger charg-



DISTILLING PEPPERMINT OIL BY SEIRO (OLD TYPE OF STILL) AT NOTSUEUSHI FARM

ing, less labor for charging and discharging than the still referred to before. On the other hand, it has the following defects: the distillation is incomplete on account of some oil remaining in the "Seiro;" besides, the life of the still is only about four years.

(4) By the hanging vat. The "Seiro" has been lately improved and provided with a false bottom of metal netting, the other parts remaining the same. At the end of the distillation the still (Seiro) is hoisted by means of a rope attached to a series of pulleys and then the distillation residue is discharged. The operation was made easier by the use of this kind of improved still. Such use of the hanging vat is said to have additional advantages; namely, the charge of material is larger, discharging easier and durability prolonged (about ten years). The author thinks that it is the best type of still employed among the distillers of peppermint oil.

As a receiver, the so-called "Mizukiri-Kame" is employed, which is a pot of stoneware with a small opening on the bottom. The pot stands in the beginning of distillation, in a small trough filled with water. As the oil distills and accumulates in the pot, water in the pot is gradually displaced through the opening on the bottom into the trough until finally the entire

pot is filled with oil and then it can be removed by closing the opening with a finger tip while under water. Water in the trough is made to flow back into the kettle from time to time for replenishing it.

As a rule, the end of a distillation is determined by practice from the appearance of the distillate dropping into the receiver. In this way one entire process is carried out in about three hours, charging and discharging requiring each about thirty minutes. Such distillations are usually repeated three or four times per day.

The crude oil is separated from water, filtered and then put into cans. Two cans are packed as one set, in a box. The product is sold to commission merchants or directly to exporters and through those channels it is exported from Yokohama or Kobe. The separation of menthol is carried on in the hands of exporters before the goods are shipped either to Europe or America. The distillation residue is used as forage for domestic animals or is burned in order to save the ash as fertilizer.

IMPERIAL TOKYO UNIVERSITY
CARE PROF. T. KAMOI
JAPAN

ON JAPANESE PEPPERMINT OIL

By YEINOSUKE SHINOSAKI

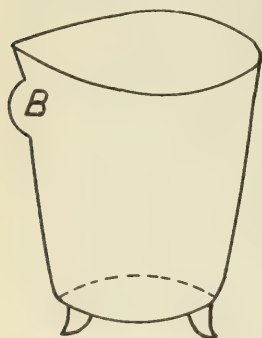
Received May 24, 1913

The peppermint oils examined by the author are those which are produced at the Kitami Branch of the Agricultural Experiment Station of Hokkaido and the Odakōgetsu Peppermint Oil Trade Association in the Okayama prefecture.

I. HOKKAIDO PEPPERMINT OIL OF ENGLISH AND GERMAN ORIGIN

Peppermint of Mitcham, England and Hamburg, Germany which were imported into Japan a few years ago, have been put on trial cultivation and dis-

	Year	German origin	Japanese origin (Kitami-Akamaru)	English Origin
Plantation.....	1910	Nov. 10		
	1911	May 12		
Germination.....	1910	May 26	May 23	May 25
	1911	June 1	May 7	May 5
Flowering.....	1910	Sept. 4	May 7	Sept. 4
	1911	Sept. 7	May 7	Sept. 13
Cutting.....	1910	Sept. 23	May 7	Sept. 13
	1911	Sept. 16	May 7	Sept. 13
Length of peppermint at cutting time.....	1910	53.93 cm.	88.48	57.27
	1911	79.08 cm.	62.42	66.05
Weight of cutting per 1 ton (0.245 acre).....	1910	421.1 kg.	559.1	771.0
	1911	1716.6 kg.	1161.2	1158.3
Weight of dried herb per 1 ton.	1910	124.13 kg.	143.0	214.88
	1911	399.9 kg.	199.57	279.15
Weight of oil from dried herb per 1 ton.....	1910	975 grams	787.5	2625
	1911	255.0 grams	1687.5	2775
Yield of oil.....	1910	0.79%	0.52	1.23
	1911	0.63%	0.84	0.99



RECEIVER "MIZUKIRI-KAME"

tillation at the Katami Branch. Mr. S. Yanada, Director of the Branch, has published the foregoing results of the trial.

The results determined by the author are as follows:

	German origin		Japanese origin	English origin	
	1910	1911		1910	1911
D ₁₅	0.9638	0.9105	0.8989	0.9228	0.9132
N _D ²⁰	1.6117	1.4672	1.4602	1.4717	1.6573
α _D	—42.25		—28.92	—52.25	—63.60
Acid No.....	19.53	Nil	Nil	4.42	7.06
Menthyl acetate, per cent.....	24.94	11.08	6.35	26.50	13.65
Ester menthol, per cent.....	19.65	8.69	5.00	20.88	10.75
Free menthol, per cent.....	66.06	57.61	64.30	66.00	64.65
Total menthol, per cent.....	85.71	66.30	69.30	66.88	75.60
Solubility (70% alcohol at 20° C.).....	2.5 vols. insol. in 15 vols.		2.8 vols. insol. in 15 vols.	3 vols.	

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
D ₁₅	0.9005	0.9012	0.9010	0.8991	0.9010	0.9020
N _D ²⁰	1.4600	1.6599	1.6602	1.4600	1.5598	1.6607
α _D	—33.75°	—32.50°	—31.80°	—24.00°	—33.60°	—39.60°
Acid No.....	Nil	Nil	0.7	1.45	2.00	Nil
Menthyl acetate, per cent.....	2.79	4.70	4.32	3.68	3.31	5.20
Ester menthol, per cent.....	2.2	3.7	3.6	2.9	2.61	4.10
Free menthol, per cent.....	69.23	66.52	68.20	66.20	66.26	70.10
Total menthol, per cent.....	71.43	70.22	71.60	69.10	68.85	74.10
Solubility (70 per cent alc. at 20° C.).....	2.6 vols.	2.5 vols	2.7 vols	2.7 vols.	2.8 vols.	2.5 vols.

II. OKAYAMA PEPPERMINT OIL OF GERMAN ORIGIN

German peppermint has a reddish violet stem and its leaf is longer than that of Japanese origin. The oil examined by the author was obtained from the production in 1909. The distillation was carried out from the end of June to the beginning of July, 1910, and the yield of oil was only 0.8 per cent, while that of Japanese peppermint is 1.6 per cent. The oil is dark brown and has a sweet taste. In the following table of the author's experimental results, the nature of the oil of Japanese origin is given for the comparison:

	German origin	Japanese origin
D.....	0.9161 (15° C.)	0.8977 (24° C.)
α _D	—18.15	—40
Acid No.....	3.45	2.8
Sap. No.....	33.46	13.85
Ester No.....	30.01	11.08
Free menthol, per cent.....	36.07	79.14
Ester menthol, per cent.....	8.36	2.06
Total menthol, per cent.....	58.61	82.23
Solubility (70 per cent alcohol at 20° C.).....	Insol.	3 vols.

The analyses of other samples which were produced in 1911 (the yield of oil is unknown) are:

	A	B
D ₁₅	0.9035	0.9140
N _D ²⁰	1.6610	1.6667
α _D	—34.02	—54.75
Acid No.....	0.81	Nil
Menthyl acetate, per cent.....	4.30	8.11
Ester menthol, per cent.....	3.46	6.39
Free menthol, per cent.....	75.76	46.55
Total menthol, per cent.....	79.20	52.94
Solubility (70 per cent alcohol at 20° C.).....	2.9 vols.	Insol. in 15 vols.

III. HOKKAIDO PEPPERMINT OIL OF JAPANESE ORIGIN

1. OIL FROM HERBS DRIED BY VARIOUS METHODS.—The experiments carried out at the Kitami Branch

to determine the yield of oil by the various drying methods are as follows:

	Cutting time	Kg. of dry herb from 375 kg.		Grams of oil from 37.5 kg.	
		Cuttings	Dry herbs	Cuttings	
No. 1. Drying on shelf (out of doors).....	Sep. 24	96.87	662.50	135.00	
No. 2. Drying on roof forming shelf (out of doors).....	Sep. 24	97.88	300.00	78.75	
No. 3. Drying by hanging in series of sheaves under the eaves of north direction.....	Sep. 24	92.13	318.75	78.76	
No. 4. Drying on shelf indoors (under direct sunlight).....	Sep. 24	81.62	251.25	56.25	
No. 5. Drying by hanging in series of sheaves indoors (under direct sunlight).....	Sep. 24	...	375.00	82.50	
No. 6. Drying by hanging in series of sheaves indoors (in the shade).....	Sep. 24	98.76	453.76	120.00	

The properties of the oil are found as follows:

	No. 3	No. 4	No. 5	No. 6
D ₁₅	0.9010	0.8991	0.9010	0.9020
N _D ²⁰	1.6602	1.4600	1.5598	1.6607
α _D	—31.80°	—24.00°	—33.60°	—39.60°
Acid No.....	0.7	1.45	2.00	Nil
Menthyl acetate, per cent.....	4.32	3.68	3.31	5.20
Ester menthol, per cent.....	3.6	2.9	2.61	4.10
Free menthol, per cent.....	68.20	66.20	66.26	70.10
Total menthol, per cent.....	71.60	69.10	68.85	74.10
Solubility (70 per cent alc. at 20° C.).....	2.7 vols	2.7 vols.	2.8 vols.	2.5 vols.

2. LEAF AND NORMAL OIL.—The report on the yield of the two kinds of oil at the Kitami Branch is:

Weight of oil from 375 kg. of dried herb.....	322.5 kg.
Weight of oil from 375 kg. of dried leaf.....	217.5 kg.

The analytical results are:

	D ₂₀	N _D ²⁰	α _D	Acid No.	Menthyl acetate Per cent	Ester menthol Per cent	Free menthol Per cent	Total menthol Per cent
Normal oil.....	0.8982	1.4607	—34.00°	1.53	4.10	3.23	78.17	81.40
Leaf oil.....	0.9028	1.4600	—33.33°	1.04	4.56	3.51	67.91	71.41
Solubility (70 per cent alcohol at 20° C.).....	Normal oil 2.6 vols							Leaf oil 2.6 vols.

3. FALLEN LEAF OIL.—The oil obtained by the distillation at the Katami Branch has a pale yellow color.

	D ₂₀	N _D ²⁰	α _D	Acid No.	Per cent	Ester menthol Per cent	Free menthol Per cent	Total menthol Per cent	Solubility (70 per cent alc. at 20° C.)
Normal oil.....	0.9000	1.6600	—21.15°	0.76	13.44	75.59	75.37	85.96	2.6 vols.

4. COMMERCIAL PEPPERMINT OIL.—(a) *Normal Oil*. The oil examined by the author (its origin is unknown), perhaps of Hokkaido, has a pale brown color.

	D ₂₀	N _D ²⁰	α _D	Acid No.	Per cent	Ester menthol Per cent	Free menthol Per cent	Total menthol Per cent	Solubility (70 per cent alc. at 20° C.)
Normal oil.....	0.9000	1.6601	—33.85°	2.18	3.18	3.0	71.20	74.20	2.8 vols.

(b) "*Peppermint Oil*" and "*Purified Peppermint Oil*."—The samples which were presented at the Gummi-Competitive Exhibition in 1910 had the following constants:

	Peppermint oil	Purified peppermint oil
D ₂₀	0.9010	0.8990
n _D	1.4886	1.4879
sp	89.60	87.40 ¹
Acid No.	1.82	3.60
Methyl acetate, per cent	9.00	11.47
Ester menthol, per cent	7.16	9.03
Ester menthyl, per cent	58.04	48.38
Total menthol, per cent	65.20	57.41
Solubility 10 per cent alcohol at 20°C	3 vols.	3 vols.

IMPERIAL TOKYO UNIVERSITY
CARE PROF. T. KAMOI
JAPAN

THE USE OF THE IMMERSION REFRACTOMETER IN EXAMINING AMERICAN BEERS MADE FROM MALT AND UNMALTED CEREALS¹

By ROBERT SCHWARTZ

The application of the immersion refractometer to the analysis of numerous chemical solutions and food products has attracted the attention of many investigators, and during the past 12 years quite a few analytical methods based upon the use of this instrument, together with valuable tables, have been published in various chemical journals. A considerable part of this work has been done by fermentation chemists, who quickly recognized the fact that the immersion refractometer was especially well adapted for the analysis of the products obtained by the wine grower, the distiller and the brewer. It is to the work done in the last mentioned field that the author desires to call special attention.

Tornøe,² in 1897, published a method for the analysis of beer which was partially based upon determining the index of refraction, using sodium light and a specially constructed type of differential refractometer. This method, while fairly rapid and quite accurate, did not, however, find wide application.

The introduction of the Zeiss immersion refractometer, which is so extremely simple to manipulate, gave fresh impetus to the study of optical methods for the examination of liquids such as beer. In 1903, Ackermann and Spindler³ published a method for determining the extract by the formula $E = (J - J') / 6750$, in which J = index of refraction of the beer, J' = index of refraction of the distillate, and 6750 an empirically determined factor. In this method the index of refraction of the beer and the distillate are calculated from the immersion refractometer reading of these liquids.

In 1905 Ackermann⁴ constructed a calculating machine with which to determine the percentage of alcohol and extract in beer from the density of the decarbonated beer, taken at 15/15° C. and its refractometer reading at 17.5° C. It is not the purpose of this paper to discuss the above publication other than to say that this method is far simpler and much more rapid than the official pycnometer analysis. Ackermann

carefully tested the accuracy of the method by having different analysts send him small samples of beer, together with a statement of their density. From this and the refractometer reading taken by himself, Ackermann calculated the percentage of alcohol and extract with the aid of his machine. Some of the results obtained are discussed below. It must be stated that this calculating apparatus was based upon tables which had been worked out from analytical data obtained by means of the pycnometer, and the corrected alcohol and extract tables of Karl Windisch.⁵

During the same year Barth² published a formula for determining the extract and alcohol in beer from the specific gravity and the refractometer reading of the same. In his article Barth published the results of 16 analyses, and to these we shall again refer below.

In 1910 Danzer³ published a series of tables (also based upon the alcohol and extract tables of Karl Windisch) from which the alcohol and extract of any beer could be calculated from the same determinations as those used in Ackermann's method. As these tables are quite readily accessible, and the calculations involved very simple, they put the refractometric method of beer analysis within the reach of all chemists.

The results published by Ackermann,⁴ and also those given by Barth,⁵ show but small differences between the percentage of alcohol and extract as determined by the refractometer and the pycnometer. It is therefore somewhat surprising that the former method has not come into more general use by brewing chemists. Particularly here in America, has the immersion refractometer failed to receive from the brewing chemists the attention which it so justly deserves.

Although the author has never found any direct written statement to the effect that the method, as published by Ackermann, could not be applied to typical American beers which are brewed from a mixture containing 60-70 per cent malt and 40-30 per cent adjuncts (in most instances unmalted cereals), some of our brewing chemists have informally expressed the belief that the results obtained with the refractometer on such American beers would not be sufficiently accurate to permit the use of this instrument.

The writer, therefore, decided to investigate this matter and examined, with the aid of the refractometer and the Danzer tables, 47 samples of beer and ale which were also analyzed by another chemist, using the official method, namely, distillation and determination of the specific gravity of the distillate and residue with the pycnometer. Attention must be called to the fact that in calculating the percentages of extract and alcohol equivalent to the various densities found, the tables of Karl Windisch, and not those given in Bulletin No. 107, revised, Bureau of Chemistry, U. S. Dept. of Agriculture, were used.

¹ Paper presented before the New York Section of the American Chemical Society, Chemists' Club, June 6, 1913.

² *Z. f. d. ges. Brauwesen*, **20**, 373 (1897).

³ *Ibid.*, **26**, 441 (1903).

⁴ *Z. f. d. ges. Brauwesen*, **28**, 33 (1905).

⁵ These tables have been published in numerous journals and text books.

² *Ibid.*, **28**, 303 (1905).

³ *Z. f. d. ges. Brauwesen*, **32** (1910).

⁴ See reference 3.

⁵ See reference 4.

The table for extract in beer, by H. Ellion, given in this Bulletin, gives the same values as the official Balling table, but as the figures in the latter are 0.07 per cent higher than those found in the Windisch table, a correction of -0.07 per cent. in the extract as determined by the refractometer must be made when using either the Ellion or Balling table to convert the specific gravity to percentage of extract by weight. The alcohol table of Gilpin, Drinkwater and Squibb¹ is about 0.02 per cent lower than that of K. Windisch, and therefore the use of the former

warmer months, however, it was found necessary to cool the water bath slightly under 17.5° C. and start taking the refractometer readings when the beers had reached the above temperature. During the time required for testing the samples, the temperature rarely increased more than 0.5° C. The readings were then corrected for an average temperature deviation of 0.25° C., which, according to Stanek and Miskovsky,² involves an addition of 0.05° of the refractometer scale. As 0.1° Ref. is equivalent to 0.006 per cent extract, or to 0.026 per cent alcohol,

TABLE I

Laboratory number	Specific gravity 15/15	Refractometer reading at 17°	Alcohol by pycnometer	Alcohol by refractometer	Difference in 1/100 per cent		Extract by pycnometer	Extract by refractometer	Difference in 1/100 per cent		Original gravity pycnometer analysis	Original gravity refractometer analysis	Difference in 1/100 per cent	
					+	-			+	-			+	-
1	1.01262	42.45	4.26	4.45	+	19	5.05	5.03	+	2	13.25	13.60	+	35
2	1.01146	37.65	3.35	3.42	+	7	4.85	4.37	+	12	12.45	12.50	+	5
3	1.01216	41.00	3.94	3.90	+	4	4.37	4.97	+	...	10.85	10.95	+	10
4	1.00488	34.80	4.25	4.29	+	4	3.11	3.17	+	6	11.30	11.45	+	15
5	1.01222	42.00	4.03	4.09	+	6	4.85	4.77	+	8	12.65	12.65	+	...
6	1.01642	45.40	3.83	3.95	+	12	5.75	5.95	+	20	13.15	13.55	+	40
7	1.01642	42.40	3.10	3.19	+	9	5.53	5.61	+	8	11.50	11.75	+	25
8	1.01648	43.00	3.30	3.30	+	0	5.59	5.66	+	7	11.95	12.05	+	10
9	1.01762	45.35	3.76	3.62	+	14	6.03	6.10	+	7	13.30	13.10	+	20
10	1.02088	46.60	3.17	3.08	+	9	6.54	6.66	+	12	12.65	12.60	+	5
11	1.01190	40.10	3.80	3.74	+	6	4.68	4.72	+	4	12.00	11.95	+	5
12	1.01534	44.35	3.89	3.95	+	6	5.52	5.69	+	17	13.05	13.30	+	25
13	1.01924	46.05	3.29	3.36	+	7	6.32	6.39	+	7	12.70	12.85	+	15
14	1.01296	41.45	3.97	3.82	+	15	5.01	5.02	+	1	12.65	12.40	+	25
15	1.01146	37.40	3.18	3.15	+	3	4.31	4.33	+	2	10.45	10.40	+	5
16	1.01554	41.70	3.25	3.20	+	5	5.31	5.38	+	7	11.60	11.60	+	...
17	1.00458	34.55	4.15	4.20	+	5	3.05	3.10	+	5	11.05	11.20	+	15
18	1.01582	42.75	3.43	3.38	+	5	5.50	5.56	+	6	12.10	12.10	+	...
19	1.01384	40.05	3.36	3.20	+	16	4.96	4.97	+	1	11.45	11.15	+	30
20	1.01394	40.25	3.77	3.74	+	3	5.12	5.20	+	8	12.40	12.40	+	...
21	1.01726	42.75	3.06	3.03	+	3	5.73	5.73	+	0	11.65	11.60	+	5
22	1.01278	41.35	3.79	3.85	+	4	4.92	4.99	+	7	12.25	12.40	+	15
23	1.01434 (a)	4.07	4.04	3	+	3	5.36	5.48	+	12	13.20	13.25	+	5
24	1.01110 (a)	4.14	4.08	6	+	6	4.67	4.68	+	1	12.65	12.55	+	10
25	1.01838 (a)	3.66	3.59	7	+	...	6.18	6.28	+	10	13.25	13.20	+	5
26	1.01542	41.60	3.19	3.21	+	2	5.36	5.35	+	1	11.50	11.55	+	5
27	1.01532	41.60	3.23	3.23	+	0	5.34	5.35	+	1	11.55	11.55	+	...
28	1.01822	46.60	3.79	3.96	+	17	6.33	6.26	+	7	13.65	13.90	+	25
29	1.01246	39.25	3.37	3.37	+	0	4.64	4.68	+	4	11.15	11.20	+	5
30	1.01158	37.25	3.15	3.07	+	8	4.30	4.33	+	3	10.40	10.25	+	15
31	1.01250	40.50	3.78	3.69	+	9	4.81	4.85	+	4	12.10	11.95	+	15
32	1.01024	38.55	4.00	3.87	+	13	4.35	4.32	+	3	12.05	11.80	+	25
33	1.01174	41.00	4.22	4.02	+	20	4.78	4.82	+	4	12.90	12.60	+	30
34	1.01320	41.85	4.03	3.86	+	17	5.03	5.11	+	8	12.80	12.55	+	25
35	1.01472	42.85	3.83	3.73	+	9	5.33	5.42	+	9	11.70	11.60	+	10
36	1.01392	41.50	3.58	3.58	+	0	5.06	5.15	+	9	12.05	12.15	+	10
37	1.01260	41.95	4.14	4.04	+	10	4.98	5.04	+	6	13.00	12.85	+	15
38	1.01700	42.85	3.32	3.12	+	20	5.69	5.71	+	2	12.10	11.75	+	35
39	1.01394	43.70	4.31	4.17	+	14	5.31	5.42	+	11	13.25	13.10	+	15
40	1.01462	42.65	3.60	3.70	+	10	5.31	5.38	+	7	12.25	12.50	+	25
41	1.01256	42.05	4.15	4.08	+	7	4.97	5.05	+	8	12.95	12.90	+	5
42	1.01188	39.60	3.68	3.61	+	7	4.61	4.65	+	4	11.70	11.60	+	10
43	1.01078	39.15	3.90	3.78	+	12	4.38	4.46	+	8	11.90	11.75	+	15
44	1.01842	45.35	3.45	3.41	+	4	6.17	6.20	+	3	12.80	12.80	+	0
45	1.01550	42.30	3.33	3.37	+	4	5.40	5.45	+	5	11.80	11.95	+	15
46	1.01752	43.55	3.21	3.07	+	14	5.83	5.86	+	3	12.00	11.80	+	20
47	1.01462	40.45	3.20	3.12	+	8	5.04	5.11	+	7	11.20	11.15	+	5

(a) Figures for refractometer readings were lost after results had been calculated.

table requires a correction of +0.02 per cent in the refractometer results. The water bath used in at-temperating the decarbonated beers was a large, felt-jacketed enameled pot into which was inserted a revolving umbrella frame capable of holding 12 small beakers. During the winter and spring the temperature at the surface of this water bath would remain unchanged long enough to attemperate the 12 beers and take their refractometer reading. During the

the error in the case of the extract is entirely negligible, and in the case of the alcohol so small as to be of practically no importance for commercial or technical analyses.

The results of the analyses of the 47 beers and ales are given in Table I.

Of these samples, Nos. 11, 12 and 13 were beers made from barley malt and hops only; samples Nos. 4, 17, 32 and 39 were top fermented ales, and all the

¹ Bull. 107, revised.

² Z. f. d. ges. Brauerei, 33, 145 (1910)

rest typical American beers. The last named, as well as ale No. 30, were brewed from malt and malt adjuncts. Most of these samples were of pale yellow color, but several were of the dark amber type, such as we find in the domestic "Muenchener Style" beer. The darker beers of the "Wuerzburger Type," as well as porter and stout, could not be tested without considerable dilution, and as time was not available to investigate the effect of this procedure on the final results, no very dark beers or ales were taken.

The above figures show the following maximum, minimum and average differences between the results obtained by the official (pycnometer) and the refractometer method.

(In calculating the original gravity, the formula $G = 1.93 A + E$ has been used, and the results rounded off to the nearest 0.05 per cent.)

	Maximum Per cent	Minimum Per cent	Average Per cent
Extract.....	0.20	0	0.063
Alcohol.....	0.20	0	0.081
Original gravity (calculated).....	0.40	0	0.140

While the maximum deviation may seem somewhat large, it must be remembered that the examinations of these beers, both with the refractometer and the pycnometer, were made as regular routine analyses, and that therefore these maximum figures can be accepted as the largest variations likely to result. The differences cannot be entirely attributed to error in the refractometer method, for the results obtained with the pycnometer under the above conditions also involved an error of ± 0.05 per cent.

In order to compare the above differences between the pycnometer and the refractometer method, the average differences found by Ackermann¹ and by Barth² have been tabulated with those given above:

	Extract	Alcohol	Original gravity
Ackermann (44 samples).....	0.026	0.061	
Barth (16 samples).....	0.157	0.055	0.14
Author (47 samples).....	0.063	0.081	0.14

In the case of Ackermann's figures only those have been taken in which the two analyses were made by different chemists. As regards Barth's figures, all those given in his communication were taken, but it is not known whether the tests were made by different analysts. The results of Ackermann show a slightly better agreement than those of the author, but as compared with Barth, the latter figures show decidedly less deviation in the case of extract. Taken on the whole, the results must be considered as very good and as showing that, on the average, there is but little difference between the results obtained by means of the refractometer and the pycnometer.

Besides the analyses given in Table I, the refractometer was used to check the percentage of extract and alcohol by taking the refractometer reading of the distillate and beer residue. As Mohr³ had shown that for laboratory worts of 8° Balling, 1° Ball. is equivalent to 4° on the refractometer scale, and Lalin⁴ had shown

the same relationship for the products of the hydrolysis of starch in cereals, the author determined to test this relationship in regard to the beer residue left after distilling off the alcohol. That the relationship should approximately hold true was theoretically based on the fact that on the average over 75 per cent of the extract in a finished beer consists of the products of starch hydrolysis. The extract, therefore, was determined by the formula of Mohr $E = \frac{R - 15}{4}$,

where R = the refractometer reading of the residue at 17.5° C. and 15 = the refractometer reading of pure water at the same temperature.

The results obtained in this way are given below.

TABLE II—DETERMINATION OF EXTRACT IN DE-ALCOHOLIZED BEER

No.	Extract by pyc- nometer	Extract by refrac- tometer $E = \frac{R - 15}{4}$	Difference in 1/100 per cent	
			+	-
1.....	4.68	4.64	4	
2.....	5.52	5.62		10
3.....	6.32	6.30	2	
4.....	6.55	6.52	3	
5.....	5.73	5.62	11	
6.....	6.07	5.96	11	
7.....	5.01	4.94	7	
8.....	4.31	4.19	12	
9.....	5.31	5.22	9	
10.....	3.05	3.06		1
11.....	5.50	5.50	0	
12.....	4.96	4.87	9	
13.....	5.12	5.12	0	
14.....	5.36	5.39		3
15.....	4.67	4.67	0	
16.....	6.18	6.19		1

It will be noticed that the average difference in the first eight or nine analyses is considerably greater than in the later determination. This is due to the fact that the former were made in rapid succession without any correction for temperature or any time given for the prism on the refractometer to regain the standard temperature after having taken up heat from the hand of the operator who had to carefully dry the prism between the immersions. As readings at higher temperature (the temperature of the prism plays just as important a part as that of the liquid) require a plus correction, these first determinations gave low results. In the later analyses the temperature was carefully held at 17.5° C. and the prism given about 2 minutes in each beaker to regain the normal temperature.

In determining the alcoholic strength of the distillate by means of the refractometer, the table of Ackermann and Steinmann¹ was used (Table III).

In these tests the necessity of giving the prism an opportunity to regain the normal temperature is strongly brought out by the difference in the average variation in the first seven and last seven determinations, each of which series was made under the difference of conditions described above. Taking in each instance the results of the determinations made in the correct manner, it is seen that the refractometer used

with the formula $E = \frac{R - 15}{4}$ and the table of Ackermann and Steinmann, *Z. f. d. ges. Brauwesen*, 28, 259 (1905).

¹ See reference 3.

² See reference 4.

³ *Woch. f. Brauerei*, 23, 136 (1906).

⁴ *Z. f. d. ges. Brauwesen*, 32, 231 (1909).

TABLE III—DETERMINATION OF ALCOHOL IN DISTILLATES FROM BEER

Number	Alcohol by pyc- nometer	Alcohol by refrac- tometer	Difference in 1/100 per cent	
	Per cent	Per cent	+	-
1.....	4.00	3.87	13	..
2.....	4.22	3.99	23	..
3.....	4.03	3.84	19	..
4.....	3.82	3.67	15	..
5.....	4.14	4.00	14	..
6.....	3.32	3.20	12	..
7.....	4.31	4.25	6	..
8.....	3.60	3.64	..	4
9.....	4.15	4.10	5	..
10.....	3.68	3.67	1	..
11.....	3.45	3.41	4	..
12.....	3.33	3.30	3	..
13.....	3.21	3.15	6	..
14.....	3.20	3.15	5	..

mann and Steinmann checks the pycnometer quite well.

The use of the immersion refractometer for the direct analysis of beer according to the method of Ackermann or Danzer is the last question to be discussed. Do the results published herewith, as well as those made public by the authors cited, justify the adoption of the rapid, short refractometer method in place of the decidedly longer and more cumbersome pycnometer analysis? We believe that it has been shown that the agreement between the results of the two analyses is practically as good for American beers made from malt and adjuncts as it is for European all-malt beers. In Europe, it is to-day the opinion of most brewing chemists that the results obtained with the refractometer are perfectly reliable for factory control. Where questions of law, or exact food chemistry are involved, opinions differ considerably. Even in such cases, however, the variations between results obtained by the two methods rarely exceed the limits which must be permitted even in a judicial controversy. It seems, therefore, that the brewing chemist here in America is amply justified in adopting the refractometer method of beer analysis, and only reverting to the old method in legal cases or controversies between analysts.

In conclusion, the author wishes to acknowledge his thanks to Mr. Theodor Ihnen, chemist for the First Scientific Station for the Art of Brewing, for numerous beers analyzed in gathering material for this paper.

CHEMICAL LABORATORY
FIRST SCIENTIFIC STATION FOR THE ART OF BREWING
NEW YORK

CALCIUM THIOARSENATE AS A SPRAY

S. H. KATZ AND P. D. BUCKMINSTER

Received June 23, 1913

Since the inception of this work, Ellis has patented (U. S. Pat., No. 1,002,247) "a composition for agricultural spraying purposes, comprising a soluble form of alkali or alkaline earth polysulfids preferably in conjunction with a thioarsenate or other thioarsenical compound as a strengthening material and preferably with a binding or adhesive material." Parsons¹

¹ THIS JOURNAL, 4, 185.

has said of arsenic, "It is used in large quantities in combination with lead as an insecticide and it would seem worth while to have experiments inaugurated to determine if arsenic sulfid or calcium sulfarsenite, both of which are probably quite harmless to plants, may not be substituted as an insecticide, giving a much cheaper material, using more arsenic and conserving lead. It should be noted particularly that any proposed insecticide must be effective as a poison but must not injure the foliage of the plant upon which it is placed."

The above expresses in part the original purpose of this work, but it was also hoped to produce a substance which would be effective as a fungicide as well as an insecticide and scalecide, for calcium thioarsenate resembles, at least in chemical composition, the polysulfids of calcium, which, as the lime-sulfur solutions, are now used as fungicides. Calcium thioarsenate is a soluble substance, and it is well known that soluble arsenic in the arsenicals now used as sprays is injurious to foliage. But the thioarsenates are quite different in their chemical nature from the arsenites or arsenates and it was expected that there might be a corresponding difference in their physiological action on foliage. Also the thioarsenic compounds readily decompose on exposure, yielding in part insoluble arsenic trisulfid. From these considerations it was hoped that the material could be safely used as a spray. In his patent, Ellis¹ stated that his invention is particularly for the treatment of citrus trees but has to say in this regard, "Ordinarily the soluble compounds of arsenic, especially if used in effective strength for insects, have a defoliating action, but in the present case, by exposure of a solution of, for example, potassium thioarsenate, oxidation and carbonation take place more or less in the case of the polysulfid, thereby throwing out of the solution to a very considerable degree the previously dissolved sulfid of arsenic, and rendering the arsenic comparatively harmless to vegetation. This action is especially marked in the case of the polysulfid of calcium."

A solution was prepared by dissolving precipitated arsenic trisulfid in a lime-sulfur solution of 1.310 specific gravity, together with a little gelatin which seemed to aid in the solution and would serve as an adhesive when the material was sprayed. The proportion of 25 grams of arsenic trisulfid to 100 cc. of the lime-sulfur solution to 0.5 gram of gelatin agitated on a shaking machine till reaction was complete, gave on filtering a clear, deep yellow solution of 1.37 specific gravity. Exposed to air, this solution decomposed and formed a yellow gel, which, on drying, adhered tenaciously to the surface supporting it.

On analysis this solution yielded the results given in the table following. The figures for theoretical solutions of calcium thioarsenite and calcium thioarsenate having 7.51 per cent of calcium are given for comparison.

From the analyses the solute is seen to approach the composition of calcium thioarsenate which salt must be present in large quantity.

¹ Loc. cit.

	Found Per cent	Theoretical	
		Found Per cent	Theoretical Per cent
Calcium	7.51	7.61	7.51
Arsenic	9.43	9.43	9.37
Sulfur	14.24	14.29	12.01

For the figures showing the comparative fungicidal values of lime-sulfur solution and the solution of calcium thioarsenate the authors are indebted to Dr. Chas. Brooks of the United States Bureau of Plant Industry. The spore of *Penicillium glaucum* placed in a 1 per cent sugar solution to assist germination was used in the tests. The following figures are averages of duplicates and express the per cent of germinating spores after seventy-two hours. Blanks were run and in all cases gave 50 per cent germination.

PENICILLIUM PLACED DIRECTLY IN THE SOLUTIONS ON GLASS

Specific gravity of solutions	Per cent germination in lime-sulfur solution	Per cent germination in calcium thioarsenate solution
1.00125	1	None
1.000625	20	None
1.0003125	12	1

SOLUTION SPRAYED ON GLASS AND DRIED BEFORE ADDING PENICILLIUM

Specific gravity of solutions	Per cent germination on dried lime-sulfur solution	Per cent germination on dried calcium thioarsenate solution
1.01	35	5
1.005	50	None
1.0025	70	7
1.00125	65	25

The figures show that calcium thioarsenate solutions are many times more powerful as a fungicide than lime-sulfur solutions of the same density. For the latter figures for lime-sulfur solution it may be noted that the very dilute spray acts as a stimulant to germination. But since in practice the solution having a specific gravity of 1.02 to 1.04 is sprayed it has little practical bearing.

The preceding work was done in the winter when the toxic effect of the solutions on foliage under growing conditions could not be determined. In the spring, solutions of calcium thioarsenate of various densities were sprayed on new foliage of the apple tree. Solutions of 1.02 and 1.01 specific gravity killed new growth and the leaves completely. Solutions of 1.005 and 1.0025 specific gravity did not kill new growth but damaged all the leaves, killing many. Solutions of 1.00125 and 1.000625 specific gravity did not kill the leaves but damaged many of them. The solution of 1.0003125 specific gravity did only slight damage, causing small spots on some of the leaves here and there, but enough to forbid the use of even this density on apple trees. Weaker solutions were held to offer no advantages for use.

CONCLUSIONS

Calcium thioarsenate is a soluble arsenical compound that is comparatively inexpensive and that has strong fungicidal properties. It cannot be used in effective densities for spraying apple trees because

of the injury it causes to the foliage. For the spraying of plants less sensitive to arsenic than the apple tree it may be found advantageous.

CHEMICAL LABORATORY
NEW HAMPSHIRE COLLEGE
DURHAM

THE CONDITION OF SOIL PHOSPHORIC ACID INSOLUBLE IN HYDROCHLORIC ACID

By WILLIAM H. FRY¹

Received June 27, 1913

The official method² for the analysis of soils is accomplished by digesting a known quantity (10 grams) of the soil in hydrochloric acid, specific gravity 1.115, for ten hours on a steam or water bath and then analyzing the solution thus obtained for the constituents which it is desired to determine. It is almost a matter of common knowledge that this method does not invariably give the total amount of phosphoric acid present in the soil analyzed. A few figures will illustrate this. In a study of the chemical composition of Maryland soils, Veitch³ found the values given in Table I.

An examination of the foregoing table shows that in these soils from 4 per cent to 100 per cent of the total amount of phosphoric acid present went into solution in the acid used. In only two soils was the total amount extracted. The average percentage extracted is about 57.6 per cent, a little over half.

Ellett and Hill⁴ give the comparative values in Table II for various Virginia soils.

In every case except one, *i. e.*, the Coastal Plain Sandy Loam surface soil from Caroline County, the acid extraction method gave lesser amounts of phosphoric acid than the total amount obtained by the fusion method. The case in which this is not so can probably be explained by unavoidable errors of sampling. It is obvious, granting that equal amounts of phosphoric acid were present in the quantities of soil used in the two separate determinations, that the total amount cannot be less than the amount extracted by the acid digestion. This exceptional case must be discarded as proving nothing at all.

These two tables simply illustrate the fact that the official method does not always give the total amount of phosphoric acid present in the soil. There are two explanations for this. Either the phosphoric acid not extracted by the official method is present in the soil in compounds insoluble in the acid used; or else it is present in a soluble form which is protected from the action of the acid.

We have no means of directly testing the first of these possibilities. However, a comparison of Dana⁵ and Brush and Penfield⁶ resulted in the finding of

¹ Scientist in Soil Laboratory Investigations, Bureau of Soils, U. S. Department of Agriculture.

² Bureau of Chem., *Bull.* 107 (revised), pp. 14, 15 (1912).

³ Maryland Agr. Expt. Sta., *Bull.* 70 (1901).

⁴ Va. Polytech. Inst., Agr. Expt. Sta., *Bull.* 200 (1912).

⁵ "System of Mineralogy."

⁶ "Determinative Mineralogy and Blowpipe Analysis."

several mineral phosphates which these authorities state are insoluble in hydrochloric acid. Among these minerals were xenotime, an yttrium phosphate; variscite, a hydrated aluminium phosphate; lazulite, a hydrated iron-magnesium-aluminium phosphate; and others. Although none of these insoluble phosphates have been found in any of the large number of soils analyzed mineralogically by this bureau, it is still possible that some of them do occur in soils. If they do occur in soils, the quantity present must be extremely small. It is also possible that some of the insoluble phosphoric acid is present in minerals which do not carry phosphoric acid as an essential ingredient, or it may be present in other forms which the interaction in the soil solution might give rise to. As can be seen by referring to the two tables below, the quantity of this insoluble material must be very small indeed, even granting that all of the phosphoric acid not extracted by the official method is in insoluble forms.

TABLE I—PERCENTAGE OF TOTAL PHOSPHORIC ACID SOLUBLE IN 1.115 SP. GR. HYDROCHLORIC ACID. MARYLAND SOILS

Potomac clays, barrens.....	34.0
Serpentine, barrens.....	34.2
Columbian sandstone.....	64.2
Trenton limestone.....	68.0
Triassic sandstone.....	74.5
Catskill sandstone.....	4.0
Heidelberg limestone.....	61.7
Gabbro.....	100.0
Gneiss.....	69.4
Hudson River shale.....	100.0
Corn and wheat soil, eastern shore.....	60.7
Columbia, corn and wheat.....	37.5
Chesapeake, corn and wheat.....	85.0
Chesapeake, tobacco.....	62.0
Truck soils eastern shore.....	32.0
Columbia, truck, southern Maryland.....	34.2

TABLE II—COMPARISON OF TOTAL PHOSPHORIC ACID AND THAT EXTRACTED BY 1.115 SP. GR. HYDROCHLORIC ACID. VIRGINIA SOILS

	Total present	Percentages phosphoric acid extracted by 1.115 sp. gr. HCl
Limestone soil, Allegheny Co.....	0.088	0.06
Great Valley limestone clay loam.....	0.133	0.07
Piedmont bright tobacco soil, Pittsylvania Co....	0.029	0.02
Piedmont subsoil, Fairfax Co.....	0.1026	0.098
Piedmont soil, Fairfax Co.....	0.1218	0.099
Piedmont gray soil, subsoil, Appomattox.....	0.058	0.045
Piedmont gray soil, surface soil, Appomattox....	0.0826	0.074
Piedmont chocolate soil, subsoil, Appomattox Co.	0.118	0.076
Piedmont chocolate soil, surface soil, Appomattox Co.....	0.185	0.09
Piedmont "Red Lands" soil, surface soil, Albemarle Co.....	0.4048	0.113
Coastal plain sandy loam, surface soil, Caroline Co.	0.0183	0.03
Coastal Plain sandy soil, water works soil, Norfolk	0.063	0.04
Coastal Plain sandy soil, Diamond Spring soil, Norfolk.....	0.057	0.03

In regard to the second possible explanation: mineralogical analyses have shown that a very large number of soils contain apatite, a hydrochloric acid-soluble calcium phosphate, enclosed in quartz grains. Soils known to contain apatite thus enclosed in quartz were subjected to an acid digestion¹ according to the

official method; and the residues were examined mineralogically. Apatite was found still inclosed in quartz, and was apparently unattacked. This explains the insolubility of at least a large part of the phosphoric acid.

SUMMARY

There may be a very minute quantity of phosphoric acid in soils in hydrochloric acid-insoluble compounds, but a large part of the phosphoric acid not extracted is present in a soluble form, *i. e.*, as apatite, which is protected from the action of the acid.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

ANALYSES OF CONFECTIONERS' GLUCOSE¹

By EDWARD GUDEMAN

Determinations of the mineral constituents of confectioners' glucose representing over 1000 market samples examined during the years 1902 to 1913 were submitted in chart form, the curves showing the maxima, minima and averages for total ash, chlorides, sulphurous oxide and copper.

The data submitted show that no fixed ratio exists between the amounts of any of these ingredients. The chlorides, calculated to sodium chloride, approximate two-thirds of the total ash. The sulphurous oxide (SO₂) seems to increase and decrease inversely with the other ingredients, but this variation is not definite, as the age of the glucose influences the amount of sulphurous oxide present, a gradual reduction taking place.

The fluctuation in the amounts of all ingredients is so large that none of them can be taken as indicating the quality of the product, and also show that no fixed figures can be taken as standards for commercial glucose or corn syrup.

VARIATIONS IN THE MAXIMA, MINIMA AND AVERAGES

Total ash

Maxima: 84-158 parts to 10,000 parts glucose (D. S.)
Minima: 30- 50 parts to 10,000 parts glucose (D. S.)

Averages: 52- 82 parts to 10,000 parts glucose (D. S.)

Chlorides calculated to NaCl

Maxima: 68-92 parts to 10,000 parts glucose (D. S.)
Minima: 18-38 parts to 10,000 parts glucose (D. S.)

Averages: 36-56 parts to 10,000 parts glucose (D. S.)

Sulphurous oxide

Maxima: 160-340 parts to 1,000,000 parts glucose (D. S.)
Minima: 10-165 parts to 1,000,000 parts glucose (D. S.)

Averages: 60-240 parts to 1,000,000 parts glucose (D. S.)

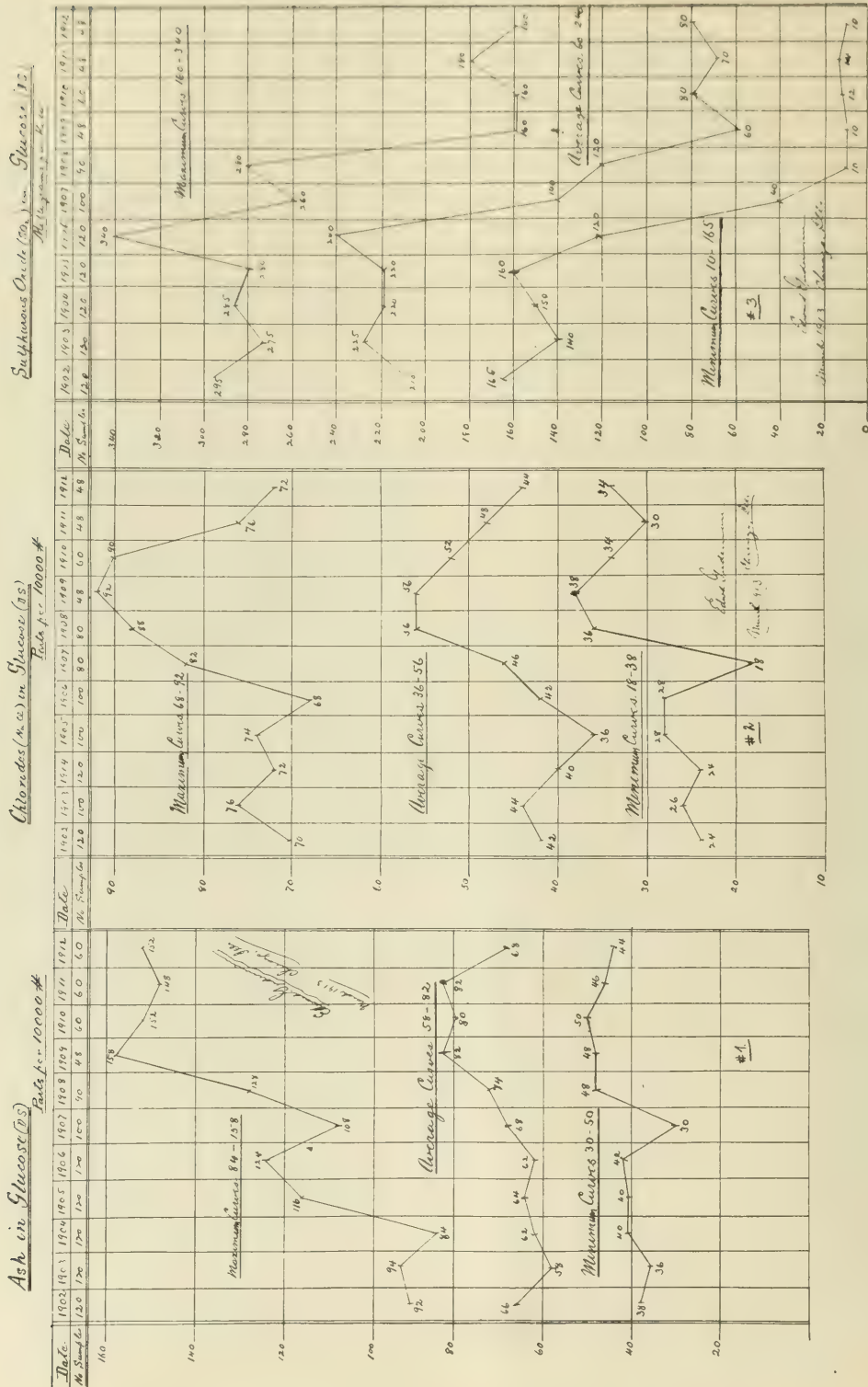
Copper

Maxima: 4-57.0 parts to 1,000,000 parts glucose (D. S.)
Minima: Trace-1.0 parts to 1,000,000 parts glucose (D. S.)

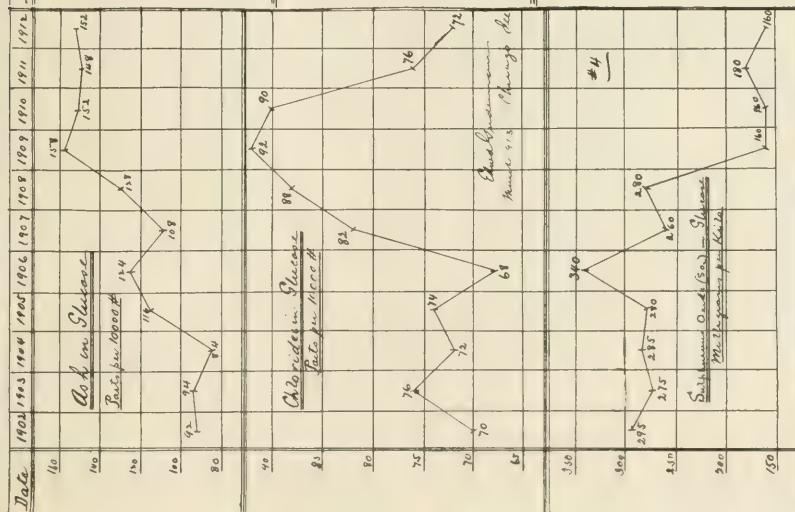
Averages: 1.5-3.5 parts to 1,000,000 parts glucose (D. S.)

¹ The acid digestions were made by Mr. R. F. Gardiner, of this Bureau.

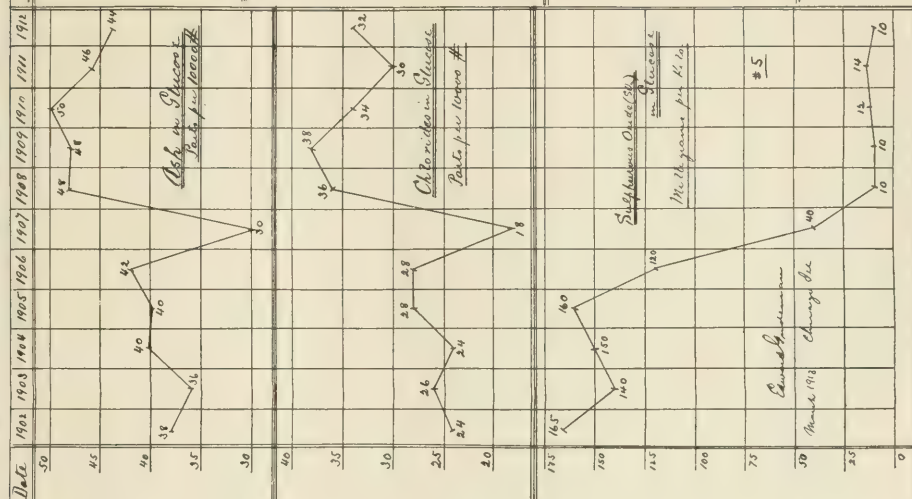
¹ Paper presented at the Milwaukee meeting of the American Chemical Society, March, 1913.



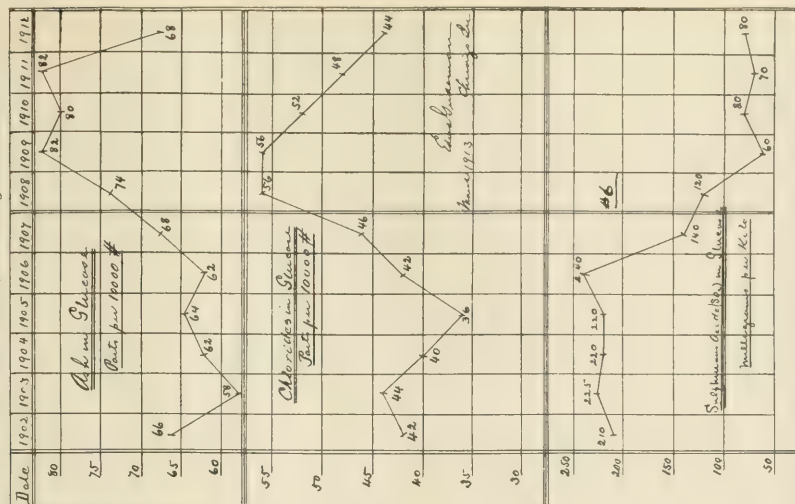
Comparison of Maximum Curves



Comparison of Minimum Curves

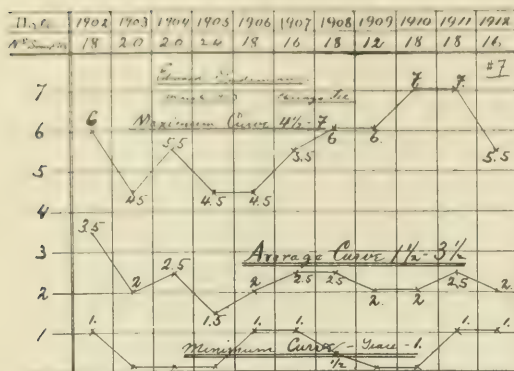


Comparison of Average Curves



Copper in Glucose (1918)

Table 1, continued



POSTAL TELEGRAPH BUILDING
CHICAGO

INFLUENCE OF OZONE ON YEAST AND BACTERIA

CARL A. NOWAK

Received May 8, 1913

To test the influence of ozone on yeast, especially as regards fermentative power, the following experiments were made:

Brewers' yeast (bottom fermenting) was freed from excess of moisture by drying on filter paper until it had the consistency of compressed yeast. Five portions of 5 grams each were then carefully weighed out into glass flasks of about 250 cc. capacity and mixed with 125 cc. of distilled water; the resulting mixture was ozonized by passing ozonized air through for periods varying from 5 to 45 minutes. The contents of the flask were then permitted to settle over night and the following morning the supernatant liquids were carefully decanted from the yeast sample, which had settled quite firmly.

To each of the yeast samples 500 cc. of clear hopped brewers' wort (sp. gr. about 1.05) were added and the samples permitted to ferment at a temperature of about 9°. Saccharometer readings were taken every second day for a period of eight days and the percentage of apparent extract (carbonic acid gas removed by shaking) tabulated.

On the eighth day each of the samples was examined microscopically for dead cells and bacteria, and the following observations were made:

The untreated sample contained the largest number of bacteria (13 per 1000 yeast cells), the treated samples (period of treatment varying from 5 to 45 minutes) contained on an average 8 bacteria per 1,000 yeast cells—the longer period of ozonization (45 minutes) showing no apparent advantage over the shorter period. The number of dead or weakened cells in the untreated sample averaged about 75 per 1,000 cells, there being practically no difference in this number in the case of the sample subjected to ozonization for a period of 5 minutes. Further increase in the duration of the treatment had, however, a positively destructive action on the yeast, the number of dead or

weakened cells in the case of 45-minute sample amounting to 200 per 1,000, or about 1/5 of the total number of cells present.

From the results in the table given below the following conclusions can be arrived at:

(1) At the outset of the fermentation the non-ozonized yeast ferments more rapidly than any one of the ozonized samples. (2) At the end of the third day the ozonized sample (5 min.) has a somewhat greater fermentative power than the non-ozonized sample, which it retains until the final degree of fermentation has been reached. (3) Inasmuch as on the fifth day and each of the following days the number of yeast cells present in the non-ozonized sample (as judged by the difference in the specific gravity of the sample with yeast and without yeast) is greater than in any of the ozonized samples, it follows that the fermentative power of the ozonized yeast must be greater than that of the non-ozonized yeast. This is most apparent in the case of the 45-minute sample in which the total number of cells had at the outset been reduced to 4/5 of the number present in the non-ozonized sample due to the prolonged period of ozonization. (4) In general, the results indicate that prolonged ozonization has an inhibitory action on the multiplication of the yeast by reproduction. (5) The maximum results as regards the destruction of bacteria and beneficial influence on fermentative power are obtained with 5 minutes' ozonization, prolonged treatment having a positively detrimental influence.

FERMENTATION TESTS

Time	Original Min.	Original Sp. gr.	2nd day Balling with yeast	3rd day		5th day		7th day	
				With-out yeast	With yeast	With-out yeast	With yeast	With-out yeast	With yeast
0	1.0524	12.86	8.35	6.20	6.45	4.65	5.15	4.05	4.75
5	1.0528	12.95	8.46	6.05	6.38	4.45	5.05	4.00	4.55
10	1.0528	12.95	8.73	6.32	6.63	4.48	4.81	4.00	4.45
20	1.0528	12.95	9.27	7.00	7.22	4.60	4.95	4.15	4.60
45	1.0525	12.88	10.86	8.85	9.00	5.58	6.12	4.25	4.75

From this it appears that the ozonization of yeast is of value, not only in freeing the yeast of objectionable organisms which are susceptible to the destructive action of ozone to a larger degree than the yeast itself, but also in eliminating the weakened cells and stimulating the fermentative power of the surviving ones. In the brewing industry the overproduction of yeast is a great source of loss, which possibly could be minimized by ozonization.

WAHL-HENIUS RESEARCH LABORATORY
CHICAGO

DETERMINATION OF SMALL AMOUNTS OF CAFFEINE A COMPARISON OF METHODS

By B. L. MURRAY

Received April 21, 1913

The object of this paper is merely to present certain interesting data that are at hand, with the thought that possibly the figures in the succeeding tables may prove useful to others having small amounts of caffeine to determine. Emphasis is placed on the fact that the comparison of methods here brought out shows that the determination of small amounts of caffeine presents a problem quite unusual, and much more

susceptible to gross errors than the determination of large amounts.

Coffees, coffee preparations, coffee extracts, coffees that have been freed from practically all of their caffeine, make up the samples used in the analyses. Wherever it was a coffee in bean or in ground condition, roasting on large scale has preceded the analysis.

The methods of analysis are those of Görtter and of Lendrich and Nottbohm. Both methods as used are given below, but it should be noted that all results here tabulated were obtained from the determinations of nitrogen in the caffeine separated from the samples, instead of by weighing the caffeine itself. No results here recorded were obtained by the alternative process of shaking out with chloroform. The work has been performed by two different analysts, thus showing the value of the methods in different hands.

TABLE I—PERCENTAGES CAFFEINE, $C_8H_{10}N_4O_2$

Sam- ple	L. & N.	Görtter	Sam- ple	L. & N.	Görtter	Sam- ple	L. & N.	Görtter
1	0.075 0.080	0.152 0.136	8	0.155 0.148	0.199 0.195	16	0.100 0.095	0.141 0.146
2	0.063 0.063	0.107 0.117	9	0.099 0.105	0.121 0.126	17	0.107 0.102	0.156 0.151
3	0.084 0.092	0.169 0.172	10	0.126 0.126	0.160 0.165	18	1.211 1.213	1.226 1.230
4	0.061 0.045	0.133 0.136	11	0.102 0.105	0.146 0.141	19	1.170 1.165	1.192 1.196
5	0.073 0.073	0.141 0.136	12	0.129 0.124	0.180 0.175	20	1.189 1.194	1.235 1.235
6	0.078 0.083	0.126 0.117	13	0.119 0.117	0.169 0.165	21	0.049 0.044	0.083 0.078
7	0.598 0.596	0.627 0.618	14	0.124 0.119	0.151 0.141	22	0.105 0.100	0.122 0.122
			15	0.121 0.118	0.184 0.184			

It is evident from Table I that the Görtter method gives results greatly at variance with and higher than those of Lendrich and Nottbohm. This variation, as will be seen, becomes pronounced when, as a rule, less than 0.5 per cent of caffeine is at hand. One must, therefore, select his method of analysis

TABLE II—PERCENTAGES CAFFEINE

Sample	L. & N. method		Sample	I. & N. method		Sample	I. & N. method	
	Complete	Without $KMnO_4$		Complete	Without $KMnO_4$		Complete	Without $KMnO_4$
23	0.185 0.178	0.189	26	0.143 0.146	0.168	29	0.143 0.138	0.175
24	0.129 0.119	0.175	27	0.131 0.127	0.153	31	0.112 0.112	0.158
25	0.148 0.146	0.156	28	0.126 0.122	0.141	32	0.168 0.178	0.197
			29	0.212 0.211	0.216	33	0.143 0.143	0.204

with care because differences of fifty and one hundred per cent are not uncommon.

Some experiments have been made with the idea

of ascertaining the value of the purification of the crude caffeine by means of potassium permanganate as used by Lendrich and Nottbohm. The few results in Table II show the effect of the purification.

From Table II the necessity of the permanganate purification as described by the authors of the method is confirmed, and in addition the effect and extent of the purification is brought out.

Table III is presented merely to show the nature of results obtained by the Lendrich and Nottbohm method, that is, mainly, how duplicate analyses agree.

TABLE III—PERCENTAGES CAFFEINE—DUPLICATES BY L. & N. METHOD

Sample	Sample	Sample	Sample
34 0.165 0.162	40 0.131 0.126	45 0.131 0.136	50 0.151 0.151
35 0.199 0.210	41 0.159 0.172	46 0.132 0.134	51 0.097 0.102
36 0.612 0.626	42 0.137 0.148	47 0.160 0.155	52 0.131 0.114
37 0.124 0.124	43 0.155 0.151	48 0.155 0.160	53 0.055 0.068 0.058
38 0.180 0.206	44 0.151 0.151	49 0.117 0.112	54 0.136 0.138
39 0.130 0.140			

GÖRTER METHOD

Moisten 11 grams of the finely powdered coffee with 3 cc. of water, allow to stand for half an hour, and extract for three hours in a Soxhlet extractor with chloroform. Evaporate the extract, treat the residue of fat and caffeine with hot water, filter through a cotton plug and a moistened filter paper, and wash with hot water. Make up the filtrate and washings to 55 cc., pipette off 50 cc., and extract four times with chloroform. This chloroform extract is evaporated in a tared flask and the caffeine dried at 100° and weighed.

Calculate the caffeine from the nitrogen content also.

LENDRICH AND NOTTBOHM METHOD

Twenty grams of green or roasted coffee ground to pieces about 1 millimeter in size are moistened with 10 cc. of distilled water, thoroughly mixed, and allowed to stand 2 hours with occasional stirring. The whole is then transferred without loss into an extraction thimble and extracted with carbon tetrachloride five to eight hours in a Soxhlet apparatus. To the extracted matter about 1 gram of solid paraffin is added, then the carbon tetrachloride is completely distilled off and the remaining residue extracted four times with boiling water, consisting of one portion of 50 cc. and three portions of 25 cc. each. The cooled aqueous extract is filtered upon a moistened paper and finally washed with boiling water. The filtrate cooled to room temperature is treated with from 10 to 30 cc. of a 1 per cent solution of potassium permanganate. After the permanganate has acted for fifteen minutes the excess of manganese is reduced to peroxide by the addition of a 3 per cent solution of hydrogen peroxide, containing 1 cc. of 96 per cent acetic acid in each 100 cc. The hydrogen peroxide is to be added by drops. The solution is now heated upon the water bath fifteen minutes, filtered hot, and the residue upon

the filter paper is washed with boiling water. The filtrate is evaporated to dryness in a glass evaporating dish upon the water bath, the residue dried at 100° C. for fifteen minutes, and then at once taken up with warm chloroform and filtered. The chloroformic extract is freed from chloroform and the caffeine so obtained, after drying thirty minutes at 100° C., may be

weighed. The caffeine is to be checked by determination of nitrogen.

In place of the evaporation of the aqueous caffeine solution which has been purified by permanganate, shaking out with chloroform directly may be used.

MERCK LABORATORIES
RAHWAY, N. J.

LABORATORY AND PLANT

THE DISTRIBUTION OF HEAT IN THE OPERATION OF STEAM BOILERS¹

By PERRY HARKER²

In the process of combustion of coal in boiler furnaces a comparatively large percentage of the heat in the fuel is not usefully employed for the generation of steam. The extent of the losses which ultimately affect the boiler efficiency is governed by (a) the design and physical condition of the plant, (b) the personal element in the operation of the boilers and furnaces, (c) the character and adaptability of the fuel for the plant in question, and (d) the rate of steam generation or capacity at which the boiler is operated. The efficiency with which fuel is burned is controlled by these factors, and excessive losses may be due to one or a combination of the contributing causes.

In accordance with the recent recommendations of the Power Tests Committee of the American Society of Mechanical Engineers, a balance accounting for the distribution of heat in a pound of dry coal fired consists of the following items:

- I. Heat absorbed by the boiler.
- II. Loss due to evaporating and superheating moisture in coal.
- III. Loss due to evaporating and superheating moisture formed by the combustion of hydrogen and distillation of oxygen-hydrogen compounds in the coal.
- IV. Loss due to heat carried away by dry flue gases leaving the boiler.
- V. Loss due to heat escaping through the formation of carbon monoxide (CO).
- VI. Loss due to combustible removed from ash pits and from grates during cleaning.
- VII. Loss due to superheating moisture in the air used for combustion.
- VIII. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for.

Of the items enumerated above, (IV), (V) and (VI) generally constitute about 75 per cent of the total heat which is lost in the operation of steam boilers and are the variable factors which have a direct effect on the percentage of heat imparted to the water in the generation of steam. In presenting certain data on these losses, illustrations of the origin, extent and methods which have been employed for their reduction, are submitted.

The loss which is generally the largest and in the ma-

¹ Presented at the Boston Meeting of the American Institute of Chemical Engineers, June 25-28, 1913.

² Fuel Engineer, Arthur D. Little, Inc., 93 Broad St., Boston.

jority of cases most easily reduced, is the heat carried away by the dry flue gases escaping from the boiler. Under this heading are included the sensible heat in the carbon dioxide and carbon monoxide, if any, formed by the combustion of the carbon in the fuel and the heat in the air in excess of that theoretically required leaving the boiler at the temperature of the escaping gases.

The principal causes of this loss are as follows:

(a) Improper methods of firing, which allow large quantities of air to enter the furnace either through the grates or fire doors.

(b) Condition of boiler settings. If the settings are cracked and the iron work is badly warped, a large amount of air is drawn through any openings, thereby reducing the draft available at the grate, diluting and cooling the gases as they pass over the heating surface.

(c) Poor quality of coal. Coals which contain a high percentage of ash or have a tendency to clinker cause an uneven distribution of the air through the fuel bed. When such a condition exists, large volumes of excess air enter the furnace and carry away heat in the flue gases. If the fuel is particularly fine, it will pack on the grate and produce an effect similar to that noted above.

This loss depends upon the weight of gases per pound of carbon burned together with the temperature at which these gases leave the boiler. The data which are required for this computation are the temperature of the flue gases, temperature of the boiler room, composition of the flue gases, the heating value of the coal and the carbon content of the fuel and ash pit refuse.

Several tests conducted in a plant in which the loss of heat in the flue gases was originally high are submitted in Table I. The plant in question consisted of hand-fired horizontal return tubular boilers equipped with plain grates upon which Pennsylvania semi-bituminous coal containing about 9.00 per cent of ash and 22.00 per cent of volatile matter was burned. The fires in this plant were carried at a thickness not exceeding 7 inches and were uneven, thereby permitting a very large air excess. The thickness of the fire was increased and the methods of firing were altered which resulted in a reduction of the loss of heat due to the enormous air excess from 36 to 12 per cent, with a resultant increase of about 20 per cent in the boiler efficiency. These tests afford conclusive evidence that the air excess maintained throughout the latter tests was somewhat lower than could be recom-

mended for regular operation, as it will be observed that considerable carbon monoxide was formed under the existing conditions of air supply.

TABLE I—PLANT SHOWING EXCESSIVE LOSS DUE TO HEAT CARRIED AWAY BY DRY FLUE GASES LEAVING THE BOILER

	Original conditions	Tests to effect improvement in efficiency	
1. Loss due to heat carried away by the dry flue gases.....	35.9	10.0	12.4
2. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds.....	2.7	2.7	2.8
3. Loss due to heat escaping through the formation of carbon monoxide.....	0.0	0.4	1.6
4. Loss due to combustible removed from the ash pits and from the grate during cleaning.....	3.2	7.6	4.5
Total determined losses.....	41.8	20.7	21.3
5. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for (assumed constant for all tests).....	8.9	8.9	8.9
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference).....	49.3	70.4	69.8
Total.....	100.0	100.0	100.0

The loss of heat due to the incomplete combustion of carbon to carbon monoxide is usually an important factor in studying and perfecting the process of combustion. Carbon monoxide occurs in flue gases generally accompanied by tar vapors or particles of solid carbon in the form of smoke, together with small percentages of unburned hydrogen and hydrocarbon gases. The formation of carbon monoxide is due to the following causes:

- Furnaces of poor design.
- Improper methods of firing.
- The character of the fuel, particularly with reference to the equipment in which it is burned.

While the presence of carbon monoxide (CO) shows that some heat is lost through incomplete combustion, a small percentage of this constituent generally indicates that the air excess is reduced as low as practicable. A small amount of smoke, as evidence of the presence of carbon monoxide, is a more convincing indication of economical furnace operation than a smokeless stack which may be emitting several hundred per cent of excess air.

The extent of this loss is dependent upon the percentage of carbon monoxide (CO) and carbon dioxide (CO₂) as determined by the flue gas analysis, the heating value of the coal and the percentage of carbon in the coal fired and in the ash pit refuse.

The results of several tests in a plant where loss due to unburned gases, as indicated by the presence of carbon monoxide (CO), was particularly high, are shown in Table II. The boiler equipment consisted of hand-fired vertical tubular boilers having shaking grates. Coal from the Georges Creek field, containing approximately 18.00 per cent of volatile matter, was burned. The high loss due to incomplete combustion was not attributed to the character of the coal although it had been proved that the furnace space in the boilers was not sufficient to burn coals containing higher percentages of volatile matter without the production of excessive amounts of smoke, indicating a large loss

due to incomplete combustion. Aside from the question of furnace design, the primary cause of the high percentages of carbon monoxide (CO) was the thickness of the fires. By reducing the thickness from 30 inches to 12 inches and changing the manner in which the coal was fired, the loss due to this factor was reduced from 14 to 1 per cent, with a corresponding increase in boiler efficiency.

In the operation of a boiler plant, a certain percentage of the fuel which is fed to the furnace drops through the grate and is removed from the ash pit. An additional quantity of unburned coal is drawn from the grates in hand-fired plants when the fires are cleaned. The amount of fuel lost in this manner depends on:

- The character of the coal.
- The condition of the equipment.
- The methods employed in handling the fires.

If the coal is fine or non-caking and the grates contain large air spaces, excessive amounts of fuel drop into the ash pits. Certain coals clinker badly under some conditions of operation and, therefore, during the removal of this clinker excessive amounts of unburned coal are drawn from the fires. Another cause of this loss is the frequent barring or raking of the fires when a fine or non-caking coal is used.

TABLE II PLANT SHOWING EXCESSIVE LOSS DUE TO HEAT ESCAPING THROUGH THE FORMATION OF CARBON MONOXIDE (CO)

	Original conditions	Tests to effect improvement in efficiency	
1. Loss due to heat escaping through the formation of carbon monoxide (CO).....	15.3	1.1	2.1
2. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds.....	4.1	3.8	4.2
3. Loss due to heat carried away by the dry flue gases.....	9.7	15.1	10.7
4. Loss due to combustible removed from the ash pits and from the grate during cleaning.....	3.2	3.5	3.3
Total determined losses.....	32.3	23.5	20.3
5. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for (assumed constant for all tests).....	11.2	11.2	11.2
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference).....	56.5	65.3	68.5
Total.....	100.0	100.0	100.0

The ash pit loss, which also includes the combustible removed during cleaning, is determined from the weight of this material, the percentage of combustible which it contains together with the weight of the dry coal fired. For the purpose of this computation the heating value of the combustible is taken as 14,600 B.t.u. per pound. In special cases where complete boiler tests are not made and the weights of coal and ash pit refuse are not obtained, the percentage of the heat in the fuel removed with the ash pit refuse and cleanings can be computed from the analysis of this material and the determination of the percentage of ash in the coal as fired. In calculating this item by the latter method the assumption must be made that the percentage of ash obtained by the proximate analysis of the fuel represents the inert matter

in the ash and refuse removed from the ash pits and the furnaces, that is, no account is taken of the ash which is carried off the grates and deposited in the combustion chamber, upon the water heating surface or lost up the stack. A series of tests which indicate the extent to which this loss can be reduced are submitted in Table III. This plant was equipped with inclined grate stokers upon which Pittsburg slack coal was burned. The excessive rate at which the fuel was burned in order to maintain the required capacity caused deterioration of the grates, which allowed large amounts of unburned coal to fall into the ash pits. By careful attention to grate repairs and methods of operating the stokers the boiler efficiency was increased approximately 10 per cent.

TABLE III—PLANT SHOWING EXCESSIVE LOSS DUE TO COMBUSTIBLE REMOVED FROM ASH PITS AND FROM GRATES DURING CLEANING

	Original conditions	Tests to effect improvement in efficiency	
1. Loss due to combustible removed from the ash pits and from the grate during cleaning	13.1	9.1	7.9
2. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds	3.2	3.3	3.4
3. Loss due to heat carried away by the dry flue gases	22.8	19.1	18.2
4. Loss due to heat escaping through the formation of carbon monoxide	0.0	0.0	0.0
Total determined losses	39.1	31.5	29.5
5. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for (assumed constant for all tests)	7.5	7.5	7.5
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	53.4	61.0	63.0
Total	100.0	100.0	100.0

The percentage of hydrogen in various coals is not an indication of their relative value when burned for the generation of steam. The essential feature in determining the effect of this constituent in the process of combustion is the form in which it is available in the furnace. Hydrogen, which is driven off in the uncombined state and burned by mixing with the oxygen from the air supply, is a valuable factor in the process of combustion as it develops about four times the heat generated by an equal percentage of carbon. However, a certain percentage of the hydrogen in coal is distilled from the bituminous matter in the form of tar vapor and water. The nature of these compounds has been ascertained when coal is subjected to destructive distillation, as in the manufacture of illuminating gas, but the transformation through which this portion of the hydrogen passes in the boiler furnace is as yet undetermined. For the purpose of this discussion the theory of the code of the American Society of Mechanical Engineers for conducting steam boiler trials, for the loss due to hydrogen, is accepted. This theory assumes that all hydrogen contained in the fuel, together with an equivalent amount of oxygen in the form of water, is raised from boiler room temperature, evaporated in the furnace, and is even-

tually superheated to the temperature of the escaping gases. The amount of heat lost in this manner depends upon the composition of the fuel, the temperature of the boiler room and the temperature of the escaping gases. In addition to the loss due to evaporating and superheating the moisture formed by the combustion of hydrogen and by the distillation of oxyhydrogen compounds, a small loss is incurred by subjecting the moisture in the fuel and in the air used for combustion to these processes.

Increasing interest in the economical operation of boiler plants has resulted in marked improvement in efficiency in the majority of the plants where this matter has been given careful attention. An illustration of the distribution of heat in a boiler plant which was operating with high efficiency before tests were made for contemplated improvement is shown in Table IV. This plant consisted of large units of Climax water tube boilers equipped with circular grates which were fired through a number of doors. It will be noted from the tabulation that considerable loss due to the formation of carbon monoxide (CO) occurred, but this waste is more than counterbalanced by the particularly small percentage of combustible removed from the ash pits and furnaces. The amount of combustible in this material averaged about 12 to 15 per cent, representing a fuel loss of from 0.5 to 1.0 per cent. Although the operating conditions in this plant were excellent, still greater care in the methods of firing effected an increase in boiler efficiency.

TABLE IV—PLANT OPERATING WITH HIGH EFFICIENCY

	Original conditions	Tests to effect improvement in efficiency	
1. Loss due to evaporating and superheating moisture in coal and moisture formed by the combustion of hydrogen and distillation of oxyhydrogen compounds	4.0	3.8	3.8
2. Loss due to heat carried away by the dry flue gases	14.4	10.1	11.8
3. Loss due to heat escaping through the formation of carbon monoxide	0.9	1.3	0.4
4. Loss due to combustible removed from the ash pits and from the grate during cleaning	0.6	0.8	0.9
Total determined losses	19.9	16.0	16.9
5. Loss due to unconsumed hydrogen and hydrocarbons, to radiation and unaccounted for (assumed constant for all tests)	8.0	8.0	8.0
6. Approximate percentage of heat absorbed by the boiler or boiler efficiency (by difference)	72.1	76.0	75.1
Total	100.0	100.0	100.0

The object of this article has been to indicate in a general way the problems which are encountered in determining the distribution of heat in the operation of a boiler plant. A study of the controllable losses, giving particular attention to the personal element, design and character of the equipment and quality of the fuel by the application of the principles of engineering and chemistry, can undoubtedly reduce them and effect a marked increase in efficiency.

CHEMISTRY IN RELATION TO THE FROZEN MEAT INDUSTRY OF NEW ZEALAND

By A. M. WRIGHT

Received May 20, 1913

No industry in New Zealand owes more to science than does that associated with frozen meat, and probably no science has contributed more to the success of this industry than chemistry. In every department of this important business, scientific control is exercised, not merely to maintain a high standard of quality for the products and by-products, but also to establish strict economy in manufacture, upon which the success of this trade depends. When we consider that for the year 1912 the Dominion exported 5,656,164 carcasses of mutton and lamb, it will be realized that the economic utilization of the by-products therefrom is a matter of no small concern: indeed it may be fairly claimed for this industry that the meat itself is the by-product, to such magnitude and importance have the former waste products attained.

In the earlier days of this business, the pelts and the largest portion of the viscera were buried and in many works even the blood was allowed to run to waste; gradually, however, chemistry has come into her own, and while in many instances waste occurs, yet in the larger works utilization of the various tissues and organs is carried out and rigidly controlled. A consideration of the methods of utilization and of the problems still awaiting solution may be of interest.

FROZEN MEATS

The influence of cold storage upon meats has been studied fully by Richardson and Scherubel¹ and Emmett and Grindley² on beef, and by Wright³ on lamb and mutton. These workers have shown that while certain changes occur under commercial conditions, yet these changes which are probably due to enzyme action do not affect the nutritive values, and are not bacterial. In addition to the dressed carcasses of mutton and lamb, certain organs and glands are packed and frozen for export, namely, kidneys and sweetbreads, the latter being the thymus gland. Little or no trouble has been found in keeping the sweetbread in cold storage for lengthy periods, but the kidney has been a source of frequent loss, the reason for which has not been definitely determined, but is probably due to the fact that this product is not placed soon enough in cold storage, and that incipient decomposition has ensued prior to freezing; in addition, the surfaces of the kidneys, on the outside of the boxes, have a darkened appearance and are blistered; the cause of this has not yet been discovered, but experiments in this direction are now being conducted.

OLEOMARGARINE

The abdominal fat and portion of the back and kidney fat are used in the manufacture of oleomargarine which follows American practice. At certain seasons of the year a flavor sometimes develops in this material some days or even weeks after manufacture; the odor and taste are suggestive of turnips; it

was found almost invariably to be associated with the product containing small amounts of animal tissue in suspension, when the fat was melted. Heating the fat to 160° F. and rapidly cooling it thereafter, prevented the development of the flavor and odor; the trouble was probably due to an enzyme reacting upon the albuminous material present; more careful rendering to eliminate the trace of animal tissue however remedies the trouble, which is not evident immediately after manufacture.

CASINGS

The intestines, after the removal of their contents, are cleaned, and packed with salt for export. Occasionally trouble will arise through the development of a reddish coloration due to bacteria, usually *B. prodigiosus*; this trouble is remedied by better care being exercised in the salting of the product. Sometimes the casings, after being cleaned, are frozen and shipped to Britain in this state.

TANKAGE AND BLOOD

The heads, lungs, livers, paunches, and part of the intestines together with the animals condemned as diseased are rendered in large vats for the recovery of fat; the residue, after the removal of the tallow, is pressed and dried for fertilizer. One of the problems met with in the treatment of this material is the amount of fat retained, the dried tankage containing up to 20 per cent of fat. By careful tanking and pressing not more than 15 per cent of fat need be retained, but even this amount presents a waste of no inconsiderable importance; extraction of the dried material with solvents under commercial conditions has been found to reduce the grease to 2 per cent, but up to the present no effort is being made to recover this valuable material in the above manner. The liquor from the vats after the rendering of the offal contains relatively large amounts of soluble nitrogenous material, equal to upwards of 25 per cent of the tankage produced. So far, in this country, no provision has been made for the recovery of this asset, although experiments have shown that it is a profitable undertaking. One firm, however, is installing an evaporating plant to deal with this material. The blood cooked in vats and the coagulated material, after the removal of the surplus water by wringing, is dried and mixed with the tankage. The trotter bones, after tanking, and the removal of the oil, are dried and crushed for bonedust. The fats, after recovery from the tanks, are refined and casked for export, no attempt being made to bleach the material, some of which is dark in color. The tankage and blood are used in the manufacture of artificial fertilizers in conjunction with superphosphates, potash salts, and mineral phosphate, each factory using formulae which experience has shown to give most satisfactory results for the crops and soils whereon they are applied.

WOOL AND PELTS

The skins are washed in running water to remove adhering dirt and blood. Thereafter they are placed in hydro extractors to eliminate the surplus water and are then painted on the flesh side with a suitable

¹ *J. Am. Chem. Soc.*, **30**, 1515; *THIS JOURNAL*, **1**, p. 95.

² *THIS JOURNAL*, **1**, p. 413

³ *J. Soc. Chem. Ind.*, **31**, p. 965.

mixture of sodium sulfide and lime; this loosens the wool after a few hours, depending upon the temperature. Then the wool is easily pulled off and, after classification, it is dried mechanically and packed for export. The pelts, after the removal of the wool, are washed and limed, then scudded and fleshed; after deliming in fermented bran infusion or in dilute lactic and acetic acids, they are pickled in a concentrated salt solution to which sulfuric acid has been added. Trouble has arisen in connection with the cured pelts, through the development of purple stains, and while doubtless some of these were due to iron, yet in the majority of cases the cause has been definitely traced to certain microorganisms capable of growing on pelts containing 8 to 9 per cent of salt and 0.3 per cent free sulfuric acid; experiment has demonstrated that properly cured pelts containing 12 to 13 per cent of salt and 0.5 to 0.6 per cent of free acid will withstand damage from the microorganisms, *B. prodigiosus*, which do cause purple stain in pelts not sufficiently cured.

PRESERVED MEATS

The tongues of the slaughtered animals form the chief material useful in canning, although to meet demands, considerable quantities of mutton and beef are also canned. The methods of preparation and canning follow on the whole American practice. In the curing of the meats it was found that a pure salt of 99.9 per cent purity was removing more of the soluble protein and meat bases than a salt of 97 per cent purity containing small amounts of magnesium and calcium salts, leaving the cured meats somewhat flavorless; it was found necessary to discontinue the use of the former salt on account of its purity; the influence of the impurities present in some curing salts upon the soluble matter of meat is at present the subject of investigation. The Pure Food regulations of New Zealand prohibit the use of more than 0.2 per cent of saltpeter in preserved meats.

MEAT EXTRACT

In the manufacture of this product, the material chiefly used in New Zealand is mutton; hearts and diaphragms are principally used, the material being coarsely minced and extracted in hot water, the resulting liquor, after filtration, being concentrated by open pan evaporation. It has been demonstrated that prolonged heating, such as that given in the open pan evaporation, is productive of the formation of certain bitter substances which give a "burned" flavor to the extract. These are probably peptone-like substances of which, up to 12 per cent, may be present in an extract "burned" flavor. In the preparation of an extract by rapid vacuum evaporation from a similar liquor there is found but 0.3 per cent of peptone-like substance and the "burned" flavor is absent.

CHEMICAL CONTROL

Tankage is examined for moisture, nitrogen, fat and tricalcic phosphate; blood for moisture, and nitrogen, moisture above 10 per cent being considered excessive and fat above 15 per cent indicative of faulty rendering; the amount of bone present in the

tankage determines largely the relative proportions of nitrogen and tricalcic phosphate. Mixed fertilizers are examined to ensure that they are up to the registered minimum guarantee.

Tallows are examined for titer, acidity, moisture, and ether-insoluble matter. Determinations of moisture, fat, and dirt are made on the wool samples. In oleomargarine the moisture, acidity, and foreign matter are determined as well as a note made of the "seeding," the odor, and the taste.

Meat extract is examined for moisture, salt, total nitrogen, acidity, fat, insoluble and coagulable proteids, proteoses, peptones, meat bases, and ammoniacal nitrogen. In order to ensure compliance with the pure food regulations, the amounts of potassium nitrate in preserved meats are controlled from the laboratory by frequent examinations. Pelts are examined for salt and free acid.

The water used in the preparation of the various foods is examined bacteriologically as well as chemically; the wrappers used for covering the frozen meats are examined for weighing matters, and soluble organic matter (chiefly starch) as well as being subject to test as a medium for the growth of microorganisms. The various stores used in connection with the manufacture and preparation of the products are purchased subject to control in the laboratory.

During the "off" season research work dealing with the problems met with in this industry is carried out.

CHEMICAL LABORATORY
THE CHRISTCHURCH MEAT CO., LTD.
CHRISTCHURCH, N. Z.

THE DETERMINATION OF THE MELTING POINT OF GREASES BY MEANS OF THE NEW YORK TESTING LABORATORY VISCOSIMETER

By HERMANN W. MAHR

Received May 14, 1913

The determination of the melting point of greases used for lubrication is the most important physical test made on these materials. The melting point of a grease plays the same part in judging its suitability as the viscosity does in the case of a lubricating oil.

Many methods for making this determination involving the use of a capillary tube have been devised. These methods require the grease to be melted into the tube and the tube and its contents then allowed to stand several hours, preferably over night, in order that the grease may regain its normal melting point. The exact melting point is somewhat difficult to fix by this method.

Pohl has devised the drop point method in which a thermometer bulb is covered with the grease and immersed in a water bath. We have made determinations by this method but find it hard to obtain checks, since it is difficult to decide when the grease is melted and to regulate the amount of grease on the bulb of the thermometer. Ubbelohde has modified the Pohl method and made it more exact by using a specially designed apparatus.

Gillet¹ has proposed a method which is more adapted

¹ THIS JOURNAL, 1, 352 (1909).

for the technical examination of greases. This method consists of closing the end of a glass tube of specified size of bore and length with a plug of grease 1 cm. long. This tube is then fastened to a thermometer so the plug is beside the bulb, and immersed in water with the bottom of the plug 5 cm. below the surface. The water is then heated at a given rate and the point at which the plug slides up under the water pressure is taken as the melting point. Gillett mentioned and experimented on the effect of four variable conditions which influence the results of the determination. These are the diameter of the tube, the length of the plug, the depth of its immersion, and the rate of heating. We have also noticed that, owing to the length of the tube, it is sometimes difficult to decide at just what point the plug was pushed upward; this is especially noticeable with greases of low melting points and thin consistency.

The use of the New York Testing Laboratory viscosimeter in determining the melting point of greases according to the Gillett method overcomes some of the difficulties arising through the use of the glass tube and offers other advantages. This instrument was devised by Mr. C. N. Forrest,¹ of the New York Testing Laboratory, for determining the consistency of bituminous materials. The apparatus is in two parts, a float and a conical brass collar.

The float is a deep aluminum saucer with a threaded opening in the center. The brass collar screws into the opening in the float.

The method of determining the melting point of a grease is as follows:

The brass collar is filled with the grease and screwed into the saucer. The apparatus is then floated upon the surface of the water contained in a large beaker which is provided with a thermometer whose bulb is as close as possible to the float and at the same level as the middle of the collar. The beaker should also be provided with some form of stirrer. The water in the beaker is now heated at the rate of $3-4^{\circ}$ Centigrade per minute. When the grease^c has become suffi-

ciently soft the plug in the collar will be forced out by the pressure of the water and the apparatus will sink. The temperature at which the float disappears below the surface of the water is taken as the melting point of the grease.

The melting points of several samples of grease were taken, using this apparatus, and it was possible to check these determinations to within 1° Centigrade. The melting points of these samples were also determined by the Gillett method. The results are tabulated below:

New York Testing Laboratory

Sample	Viscosimeter method		Gillett method
	Determination No. 1	Determination No. 2	
3645A.....	96° C.	95° C.	96° C.
3645B.....	95° C.	96° C.	97° C.
3645C.....	96° C.	97° C.	98° C.

The use of the New York Testing Laboratory viscosimeter for determining the melting points of greases offers a rapid accurate method. By employing it the size of the plug, the depth of its immersion, and the diameter of the tube become constants, while they are liable to vary when a glass tube is used. In addition, the melting point is indicated sharply by the apparatus sinking. The determination of the melting points of soft, low melting greases offers no difficulties by this method, since it is easy to obtain the proper sized plug and to determine the point at which it melts. When the grease melts in this apparatus it slides along on a metal surface instead of glass, thus approaching more closely conditions in grease cups and on bearings.

STANDARD TESTING LABORATORY
BOARD OF ESTIMATE AND APPOINTMENT
CITY OF NEW YORK

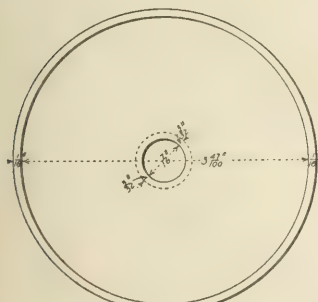
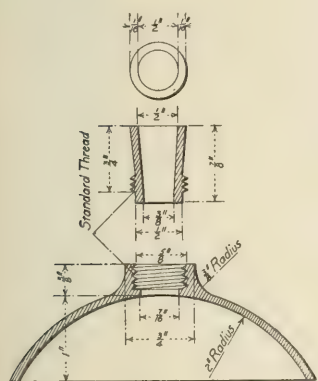
CONVENIENT DEVICE FOR ANALYTICAL IGNITIONS

By EDWARD D. CAMPBELL

Received June 9, 1913

Where students in beginning quantitative analysis do not have the use of platinum crucibles, the gravimetric determination of calcium oxide frequently presents difficulties. The precipitate of calcium oxalate may be ignited at a low heat and weighed as calcium carbonate, but in such cases the results are apt to be too low on account of partial decomposition of calcium carbonate. When an inexperienced worker depends upon complete decomposition to calcium oxide in a porcelain crucible the results are usually too high because decomposition has not been complete, or, if a blast lamp has been used, the temperature of the bottom of the crucible may become so high that the calcium oxide will attack the glaze of the crucible.

It was in order to overcome these difficulties that the combined support and protection herein described was devised for the triangle holding the crucible. These protected triangles have been in use in this laboratory for more than a year and have proven so satisfactory that it was thought a description of the method of making them would be of interest to other chemists. The use of these protected triangles has



NEW YORK TESTING LABORATORY VISCOSIMETER²

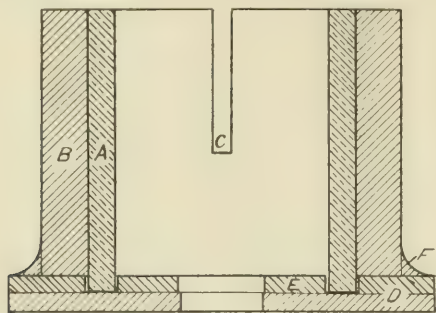
per minute. When the grease^c has become suffi-

¹ Engineering Record, 69, 584.

² Cut used with the permission of Mr. C. N. Forrest

done away with the necessity of employing blast lamps for ignitions or fusions in analytical work. The triangles can be easily made out of inexpensive material. A vertical section showing the method of construction is given in the accompanying plate.

The cylinder *A* is 7.5 cm. inside diameter, 10 cm. long, and has three equally spaced vertical slots 5 cm. deep and 6-8 mm. wide. Cylinders were, tried of



alundum, of fused silica and of fire clay such as is used for making assay muffles. The cylinders made of fire clay were found to be the most satisfactory, as they heat up a little more rapidly and give 10 to 15 degrees higher temperature than either the alundum or fused silica, and are of course much less expensive. The cylinders now in use were furnished by the Denver Fire Clay Co. The cylinder is wrapped in heavy asbestos paper cut in strips about 9.5 cm. wide until the protecting jacket *B* is about 1.5 cm. in thickness. The asbestos paper is slightly moistened with water before wrapping and when the wrapping is complete, except about one turn, the asbestos is wet with sodium silicate diluted with an equal volume of water and the wrapping completed. Care is taken to wet the outside and ends of the asbestos with one to one sodium silicate before the cylinder is allowed to dry. The asbestos wrapping is put on so that the edge of the asbestos is flush with the top of the cylinder, leaving about 6 mm. of the cylinder projecting at the bottom. When the asbestos jacket has thoroughly dried in a drying oven over night the outside of the jacket will be found quite strong and hard so that the slots in the asbestos corresponding with those in the cylinder may be cut by means of a hack saw. The triangle made of nichrome or Hoskins wire is placed in the bottom of these slots *C* and the slots are then packed with asbestos slightly dampened with water. The supporting base *D* is made of two 15 cm. pieces of asbestos board each about 6 mm. thick. The lower piece has a hole 26 to 28 mm. in diameter in the center or just large enough to admit a No. 4 Méker burner and leave an annular space of 2 or 3 mm. in width around the burner. The upper square has a hole just large enough in diameter to admit the cylinder *A* so that this latter rests directly on the lower square of asbestos and is centered by the upper asbestos square. The two squares of asbestos are well soaked with dilute sodium silicate, then cemented together by rubbing a little pure sodium silicate on the contact surfaces. After cementing together, while the asbestos

is still wet and soft, the edges are well rubbed so as to render them smooth and well knit together. While making this bottom it is best to have the asbestos on a piece of paper, then after placing another piece of paper on top the bottom should be placed between two pieces of board and dried over night in a drying oven. A small ring, *E*, of 6 mm. thick asbestos 7 cm. in diameter with a 3 cm. hole in the center is cut and placed inside the cylinder resting on the bottom *D*. This ring of asbestos is not treated with sodium silicate and is placed in position in order to prevent the downward radiated heat from affecting the lower supporting bottom. If this inner ring becomes crumbly after long use it can be easily renewed at any time by removing the cylinder, if this latter is not cemented to the base, or, if it is, by picking out the asbestos packing in the slots and removing the triangle. The base *D* is wired to a 12 cm. diameter ring belonging to a ring stand. This allows an easy vertical adjustment. It has been found convenient in a number of cases to cement the jacketed cylinder to the base in order to avoid danger of the cylinder being accidentally upset. This is easily done by means of a pulp made of asbestos scrap which has been worked up with water until completely disintegrated and the water squeezed out. The surface of the lower part of the cylinder and a little of the base near the cylinder is smeared with a little sodium silicate, then the corner is filled in with some of the asbestos pulp to which had been added some sodium silicate in order to harden it. With this pulp the corner can be filled in at *F* and after drying this will hold the cylinder and base firmly together. The burner best adapted is a No. 4 Méker, and the height of the furnace is so adjusted that the top of the burner extends 2 or 3 mm. above the asbestos ring *E* inside the cylinder.

Some tests were made to determine the efficiency of this device. One gram of calcium carbonate was placed in a No. 0 porcelain crucible, a standard platinum, platinum-rhodium thermocouple inserted in the crucible in such a way that the bead was covered with the calcium carbonate and the cover placed on the crucible. Starting with everything cold when the burner was lighted, the temperature reached within 10 or 15° C. of its maximum in from 18 to 20 minutes. The maximum recorded by the thermocouple with the cylinder open at the top was 995° C. From 950° to 975° can be easily counted on. As the temperature rose in all cases a marked slowing up was noted between 835° and 840° C., indicating the absorption of heat required for the rapid dissociation of the calcium carbonate. At the full heat of the burner the dissociation of the gram of calcium carbonate is usually complete after one hour ignition, although a second ignition to constant weight is advisable.

Determinations of the loss on ignition of limestone were made in porcelain crucibles, and it was found that results as accurate as those obtained by ignition in platinum could be easily obtained. On removing samples of limestone which had been ignited to constant weight and rinsing out the porcelain crucible with water containing a little hydrochloric acid, the porce-

lain crucible was found to be unaffected, the change in weight not exceeding 0.0001 to 0.0002 gram. The fact that the loss on ignition in limestone can be determined in a porcelain crucible with accuracy and without the crucible being attacked renders it possible to make an accurate technical analysis of limestone without the use of platinum, the silica recovered of

course not being corrected by volatilization with hydrofluoric acid. If, however, the analysis is made on the residue after the determination of the loss on ignition and the total silica does not exceed 6 or 8 per cent, the uncorrected silica recovered will be found to carry very little alumina or ferric oxide.

CHEMICAL LABORATORY
UNIVERSITY OF MICHIGAN

ADDRESSES

EFFICIENCY IN CHEMICAL INDUSTRIES¹

The Corn Products Industry

By T. B. WAGNER

During the Eighth International Congress of Applied Chemistry, held in New York in 1912, a number of general lectures were delivered, among them one by Dr. Carl Duisberg, of Germany, entitled "The Latest Achievements and Problems of the Chemical Industry." With others, I was profoundly impressed with this recital of achievements—a splendid record indeed, bearing testimony to the distinguished services rendered by the Chemist and the Chemical Engineer. It is but fair that we give the latter full credit, for while the "pure" chemist takes the initiative by developing ingenious theories and syntheses, it is the chemical engineer who follows up the former's work and transforms it into commercial success, by which is judged, in no small degree, the value to mankind of scientific effort and accomplishments. Dr. Duisberg's essay surely brought to many of us the thrill of romance, but below it all lay a deeper meaning, for it spelled the "Triumph of Efficiency." We heard, among other things, what has been done in the way of producing cheaper power with engines driven by blast furnace gas, or Mond, or even peat gas; we were told of refrigeration, where, through the means of liquid air machines, temperatures were obtained as low as minus 190° C.; of rare metals and new alloys; of electrolytic iron and refined steel; of new methods of detinning waste tin; of the production of nitrogen compounds from atmospheric nitrogen; of ammonia obtained direct from its constituent elements; of advancements in the manufacture of soda, chlorine and sulfuric acid; of the distillation of tar and of new coal tar products; of lake and coal tar colors; of synthetic perfumes and artificial silk; of pharmaceutical products and of chemotherapy; and lastly, of the brilliant results obtained in synthetic chemistry, especially in the syntheses of adrenalin and rubber.

Gentlemen, would not one have to be void of all sentiment not to be stirred when learning of such work, and not to take pride in being a member of so useful and illustrious a profession as that of Chemists and Chemical Engineers? We need not go abroad, however, to learn of the magnificent results accomplished by them, for we have abundant evidence in this country of the marvelous changes which their efficiency has brought about, with the result that this country occupies to-day a commanding position among nations in the field of applied chemistry.

"Efficiency in Chemical Industries," the subject I have chosen for this occasion, leads one, as you have seen, into such vast fields of accomplishment and possibilities, that I fear my fate to-night might be that of the parson who arose before his congregation and said: "My dear Brethren, I shall divide my sermon this morning into three parts—firstly, I shall announce my text; secondly, I shall depart from it; and thirdly, I shall never get back to it." To avoid such a calamity, the calamity of going astray, I shall speak to-day only on what efficiency has

done for the industry with which I am identified—that of Corn Products. I trust I have walked in the highways and byways of that particular domain long enough not to get lost. A further reason why I have elected to speak on this subject is that experience tells me that we rather welcome an account of accomplishments in industries other than our own, for the precedent of another's difficulties encountered and overcome, acts as a tonic to cheer us over the stumbling blocks in our own paths but they are only stumbling blocks after we have passed them and left them well behind; when they loom before us, they seem to have the proportions of mountains!

The manufacture of corn products in this country is not an infant industry, and much has been written about it, its history and evolution. The first product manufactured from corn was starch, and the first manufacturer was Thomas Kingsford, his plant being located at Oswego, N. Y. He commenced operations about 70 years ago, at a time when the raw material—Indian corn—was a low-priced commercial commodity, for in those years the population of this country was much smaller than to-day, home consumption was limited correspondingly, and a demand had not, as yet, been developed abroad. The raw material was cheap and the price of the finished product was high. The margin of profit, therefore, was considerable, and an attempt at efficiency did not appear imperative, particularly not since competitors were "few and far between." Thus the principal stimulus for efficiency was lacking. The almost exclusive aim—a commendable one—was to produce starch of the highest quality. The matter of yield and of cost was of secondary consideration. With good quality and rather handsome profits, why talk about economy or efficiency in the boiler house, in the engine room, in the transmission of power, or with respect to labor? Labor too was cheap in those days and labor unions were unknown. If the efficiency were to have been gauged, as it should among other things, by the recovery of products from a given unit, that is to say, by the yield, it cannot be denied that a manufacturer could have taken but little pride in revealing his degree of efficiency. This should not be taken as a reflection upon the industry at that time, for to be fair, we must not judge conditions retrospectively. It was the status of the industry in those days, but that the future had many and far-reaching changes in store soon became evident.

The price of corn gradually rose, and, due to growing competition, the price of the finished product declined, narrowing the margin of profit. The manufacturer, therefore, had to begin to pay attention to the subject of yield and to an increase of revenue possibly by recovering some of those products which were allowed to run to waste. First among these were the nitrogenous ingredients of corn, the "Gluten," but the method of recovery was very crude. It was collected while in a wet condition and its sale was in the nature of a local business, that is to say, it was sold to the farmers located in the neighborhood of the factory, and used by them in feeding cattle. It was not known as a commercial commodity, yet the proceeds from its sale added materially to the reduction in the cost of starch. With an increased output, the local markets eventually proved

¹ President's address before the American Institute of Chemical Engineers at the Boston meeting, June, 1913.

too small, and it became necessary to recover the gluten in a condition which would permit of shipping it to distant points. This led to the drying of the gluten, and while the recovery of this product in itself was a step in the direction of efficiency, the methods and appliances resorted to in drying were primitive. It did not take long, however, for efficiency to make its entrance; the apparatus first in use were capable of evaporating about 1000 pounds of water per hour, each unit of the apparatus employed to-day has an efficiency, expressed in terms of evaporation, equivalent to 9000 pounds of water per hour. The amount of dry gluten recovered in one of the larger factories is 250,000 pounds per day.

The hull of the corn, the "bran," underwent the same transformation, and was changed from a waste product, or offal, to a valuable staple product, the amount recovered per bushel being approximately the same as that of the gluten.

In the course of time, the manufacture of glucose was started, and the enterprise flourished. The introduction of this new product from corn furnished a splendid opportunity for the display of efficiency. In a measure, the industry was an imported one, for glucose had been made from potatoes in Germany many years prior to the establishment of the first factory in this country. In those early days it was necessary not only to import the machinery, but skilled labor as well. Among the most important were the men in charge of the vacuum pans. They were brought here at the expense of the manufacturer and engaged at extravagant salaries. They were quick to realize their advantage and soon became the "bosses" of the plant. They ruled absolutely. Their work was surrounded with great mystery, but it had to give way to efficiency, and to-day the position of a pan man is no more important than that of any other workman, in fact, unskilled men are often selected for this work and soon become experts at their posts. The problems which arose in the manufacture of glucose taxed the ingenuity and efficiency of the chemical engineer. To illustrate, I will cite the history of the Chicago Sugar Refining Company, which was organized by Chicago business men with a paid in capital of $1\frac{1}{4}$ million dollars—a large amount of money even in present-day enterprises, but particularly so in 1880, when this factory was constructed. Its purpose was the manufacture of anhydrous grape sugar (pure dextrose), the production of which, on a commercial scale, had been made possible by Dr. Arno Behr. His method differed from all previous ones in that alcohol was not required in the process of crystallization. The price of sugar was high in those days; I believe it sold at 8 cents a pound. Anhydrous dextrose, or grape sugar as it was called then, could be manufactured quite cheaply, as corn was still sold at a relatively low price. The scheme was to blend the soft cane sugar from Louisiana with this anhydrous dextrose, and sell the product to the confectioners, for whose purposes it was suited most admirably. The factory started off a great success. The product turned out was of the highest purity and called forth the commendation of every one who tried it. Thousands of barrels were sent out in the course of a few months, but in the course of another few months, the shipments commenced to be returned to the factory, because it was found that the anhydrous sugar had absorbed the moisture contained in the soft sugars, with the result that the contents of the barrels had solidified into a hard mass. It was impossible for the confectioner to use this product, and the company stood face to face with the failure of an enterprise in which, by this time, approximately $1\frac{1}{2}$ million dollars had been invested. There was no alternative but to shut down the factory. The question now arose what to do next.

Many suggestions were submitted, among them very worthy ones, but they were discarded until the chemical engineer stepped into the breach and suggested that this anhydrous sugar plant be converted into a glucose factory. I shall not go into

details, but simply recite the fact that after untold efforts and untold moments of anxiety, the new venture succeeded, and in the course of time it prospered. It may be properly said that it was principally responsible for the development of the American Industry of Corn Products, as we know it to-day.

Even though it prospered, there were many problems. Every step in the manufacture of glucose requires the most careful attention, and chemical control is needed incessantly. The aim is first to obtain the raw material—starch—in as nearly chemically pure a state as possible; this means the elimination of all nitrogenous and fatty matter, a task which offers the greatest difficulties, because of the enormous scale on which the business is conducted, because of the condition of the raw material—whether fully matured or not, whether entirely sound or slightly deficient, and even because of atmospheric conditions which exercise a certain influence. The ambition of the manufacturer is water white, crystal clear glucose, which will retain its color in all seasons, in all climates, and even if kept in transit or storage for a long period of time. Such quality depends upon a thousand and one factors, some of which it is very difficult to control. The refining of the glucose and the treatment of the refining agents are important problems, which, however, have been worked out most successfully, as the result of applied efficiency on the part of the chemical engineer.

The recovery of the gluten and the bran was an important step forward, but one of the most valuable parts of the corn was still allowed to go to waste, *viz.*, the germ, which yields the oil. There was no incentive to recover it, since no one seemed to want the oil. Had it been produced on a large scale, there would not have been a market for it, although it was realized, even in those early days, that a vegetable oil of the character of that obtained from corn must eventually become a valuable article of commerce; so it did, but it took many years of hard work to bring about this condition. Shortly before I entered the business, less than 15 years ago, they had just started producing corn oil on a large scale, but had no market for it—the oil went begging; that was a serious condition. The Chicago factory produced at that time about 15,000 pounds of oil per day, and selling as it did for less than 15 cents a gallon, the revenue from this production was but two hundred and fifty dollars. To-day the value of a gallon of corn oil is nearly 50 cents, and the amount of oil recovered from the same number of bushels as in the Chicago factory is worth \$2,700. This is not due altogether to the increased selling price, but also to the greater efficiency prevailing in the separation of the germ, and the extraction of the oil resulting in a yield 3 times larger than in the days of the Chicago factory. To-day the gross value of the oil recovered from one bushel of corn, together with that of the oil cake obtained as a by-product, is equivalent to 25 per cent of the purchase price of the corn.

The ingenuity of the chemical engineer did not stop there. The price of glycerine was rising steadily, hence the proposition suggested itself of separating the glycerine from the fatty acids. What this meant is evidenced when I recite that glycerine to-day sells at 18 cents per pound and corn oil at about $6\frac{1}{2}$ cents, and that 100 pounds of corn oil yield twelve pounds of glycerine; the price of crude oil and fatty acid is substantially the same.

To the list of by-products recovered, gluten, bran, oil cake, oil and derivatives such as glycerine and fatty acids, another was soon to be added. We still had a waste product, which, if recovered, seemed likely to be convertible into a revenue producer of the first magnitude. I am referring to the solids contained in the so-called "steep water," the water in which the corn is immersed and softened prior to grinding. It contains the most valuable ingredients of the grain, *viz.*, the organic phosphorus compounds, magnesium and potash salts, nitrogenous bodies and sugars. Many efforts had been made to recover

these solids in dry form, but owing to the hygroscopic condition of the residue, such methods were found to be impracticable. In some localities, serious consequences were the result. I have in mind the experience we had at an Iowa factory, grinding about 10,000 bushels of corn per day. The steep water was not recovered, but together with the wash waters from starch and gluten was run into a creek, which, in turn, discharged into a river of fair size. This method of disposing of the steep water soon became a menace to the plant, for proceedings were instituted in the courts with a view to having the factory shut down and declared a public nuisance because the steep water contaminated the river, killing the fish and contributing in many ways to the discomfort of the residents. The owner of the factory being unable to satisfactorily dispose of this waste, as a last resort constructed a pipe line to a farm located about 3 miles from the factory and entered into an agreement with the owner of the farm whereby he was permitted to conduct the steep water through the pipe line from the factory to the farm and discharge it there. For that privilege, besides furnishing a most excellent fertilizing material, he had to pay the farmer three thousand dollars annually. To-day we recover this former waste, by collecting it, concentrating it *in vacuo*, and adding it to the gluten feed in the form of a syrup, with which it is subsequently dried—the feed acting as an absorbent. Instead of investing in pipe lines and paying for dumping rights, the waste of a 10,000 bushel plant was thereby converted into a revenue of almost \$100,000 per year. Applied to the industry as a whole, this former waste furnishes to-day an annual gross income of approximately $1\frac{1}{2}$ million dollars.

Very little is now running to waste. Whatever small loss there is, is caused by the soluble solids carried off in the water used in the washing of starch and gluten. However, these solutions of solubles being very dilute, it is doubtful whether an efficient method will ever be devised for their recovery at a profit. It will probably be a question of economical evaporation, therefore, largely an engineering problem. Nor will the recovery of these solids add materially to the efficiency record in point of yield.

Efficiency has manifested itself in our industry in many ways. As production increased and finally exceeded the demand, ways and means had to be found for diverting the surplus into new channels. This meant partly new products and partly new markets. The latter were secured by entering our starches, for instance, into competition with products mostly foreign, such as rice, wheat, potato and cassava starch; and by studying closely the needs of the respective industries requiring starchy materials, we have succeeded, in a large measure, in replacing rice, etc., with products of corn.

The development of our products occurred simultaneously, and to the series of bulk products were added, in the course of time, a large number of special products, such as thin boiling and modified starches, suitable for every conceivable technical purpose, dextrines and gums, special varieties of glucose, mixed table syrups, so-called "70" and "80" sugars, and refined, hydrogenated and vulcanized corn oils. There is every prospect of further additions to the present number. Products of corn, in one form or another, are consumed to-day in almost every industry, and they reach every corner of the civilized world. Figuratively speaking, this branch of efficiency was raised from 1 to 100—that is to say, where originally the industry was based upon the manufacture of only one product, to wit, corn starch, to-day the number of separate articles obtained from corn presents the formidable array of 100 products and more.

Hardly anything, however, contributes so much to the general efficiency of an industry as the individual plant capacity. This is the part of our business which requires the special attention and skill of the engineer. It has been only ten years since we stopped operating those plants having a unit of only 500 bushels of corn per day. Those plants could not compete with modern

conditions for the simple reason that they did not keep pace with the demands of efficiency. How can a plant grinding 500 bushels of corn a day enter into competition with a plant converting into commercial commodities 30,000 bushels or even 50,000 bushels of corn, which is the daily capacity of the latest addition to our chain of factories, *viz.*, the mammoth plant at Argo, Illinois. It is the concentration of operations that makes it possible for this plant to carry off highest honors in point of efficiency, and this concentration is carried through every department of the plant, each department being organized as a manufacturing unit of its own. The boiler house is our steam factory. It is the business of the man in charge to manufacture and deliver steam at the lowest possible cost and if you could go through this boiler house you would be surprised, perhaps, to find to what an extent chemical control is observed, and to what extent it contributes towards the low cost of steam. The efficiency of the boiler house depends, of course, not only upon its operation, but equally as much upon the equipment; hence the old tubular boilers had to give way to modern high efficiency water tube boilers. Where formerly the standard unit was 100 H. P., it is now 600 H. P. per boiler. We now have only mechanical stokers in place of hand-fired furnaces. Great savings have been brought about in coal and ash handling machinery, so that the operation of a boiler plant to-day requires but a fraction of the labor formerly employed.

Coincident with the increased efficiency of the boiler house was the rational, the scientific use of steam. Evaporation in driers and vacuum pans is done through exhaust rather than live steam, and one may well point with pride to the fact that in spite of the large amount of exhaust steam produced, our plants are operated without the discharge into the air of a single pound of unused exhaust steam.

The engine room is another such manufacturing unit, and a high degree of efficiency is required to produce and transmit motive power at a low cost. Here the slide valve engines had to yield to the Corliss type, and more latterly to the steam turbine. The costly transmission of power by belts, rope drives and transmission shafts had to give way to electrical power. Efficiency is carried into the minutest detail; even an item apparently so small as lubricating oil did not escape the general policy of efficiency; while such items do not represent an imposing saving *per se*, the aggregate foots up a substantial amount.

The milling department is another unit of its own, and so is the refinery, the feed house, the oil plant, the dry starch house, the dextrine department, etc. Each one of these departments is in charge of a chief, responsible for the output, its quality and cost. This general efficiency is carried further in that we operate our own box and carton factories, our printing shops, barrel factories and tin can plants, which latter have a record of efficiency second to none in this country.

You will have noticed that we distinguish between two domains of efficiency: *first*, that of the Manufacturing Department; *second*, that of the Engineering Department. In the latter may be included plant construction, for efficiency not only reigns on the inside, but makes itself felt on the outside as well. Improved plant construction leads to reduction of maintenance charges, to a lowering if not elimination of fire risks, accompanied by a corresponding lowering of insurance rates, to a better safeguarding of the employees, to a reduction of accidents and to an improved sanitary condition. The last-named features, in turn, lead to increased efficiency of the workmen, without which any attempt at a high degree of general efficiency must come to naught.

Another link in the chain of general efficiency is furnished by labor-saving devices, the result of which is that less men are employed to-day in a factory grinding 30,000 bushels than were formerly required to operate a plant with a capacity of only 10,000 bushels.

Gentlemen, I have singled out the industry of Corn Products because it furnishes one of the most striking examples of what efficiency has done for the development of a chemical industry within a comparatively brief space of time. Unlike other industries, such as steel or sugar, our industry is a conglomerate of a number of others. *Per se*, the manufacture of starch has nothing to do with that of oil, the manufacture of corn syrup nothing in common with the production of concentrated feedingstuffs; the manufacture of dextrines nothing with that of dextrose, etc., yet these various departments are so related to the whole as to form inseparable parts of it, and the efficiency of the whole depends, therefore, upon the efficiency of each branch.

The net result of our efforts with respect to efficiency is perhaps best illustrated by the fact that we pay to-day for our raw material—corn—three times as much as did our predecessors, and yet we sell our products in the markets of the world at one-third of their price.

To continue the increase of this efficiency, it is necessary that we have young men with the proper training—not only men with a scientific schooling, but men who have received thorough training in engineering, who know the parts and functions of machinery and apparatus, who have a fair knowledge of factory operations, and who have a general understanding of the principles of manufacturing. It is gratifying to note that the number of colleges and universities is increasing from year to year, where a course of chemical engineering is added to the curriculum of the chemical student. The chemical industries of this country have grown from a small beginning into a position of great importance. A large share of the credit is due to the schools which furnished the men. They must give us men of ideas, men with initiative, men with mental and physical equipment to carry their creations of mind through into creations of fact. No matter how small a cog the individual may be in the big wheel of industry, he may well be proud of his share in the building up and development of the chemical industries, which contribute materially toward the prosperity of this country. If his work goes unnoticed by the public-at-large, he can find comfort in the fact that "The greatest joy of those who are steeped in work, and who have succeeded in finding new virtues and understanding the relations of things to each other, lies in work itself."

Such work cannot result other than in efficiency. Efficiency stands for all that is great and potential. Efficiency is the making of a man. Efficiency is the making of an industry. Efficiency is the making of a nation.

UTILIZING WOOD WASTE¹

By JOHN E. TEEPLE

I. INTRODUCTORY

I have been asked to give a general survey of the field of chemical wood waste utilization: what has been accomplished, what is being done, what are the prospects. In such an address many interesting details must be omitted, many subjects passed over lightly or merely mentioned; much of the material presented will be familiar to many of you, and a part to all of you.

Man has been utilizing wood from the beginning. Wherever we find him in history, even as a barbarian, he has known how to make charcoal and probably tar from wood, if he had the wood; and there was abundance of wood. Central and Northern Europe were almost entirely forest or swamp. The larger part of our own country, excluding the middle western prairies, was covered with trees. Nearly this whole state of New York, this spot on which we stand to-night, was a forest. There was no waste wood, or it was all waste, just as you choose to con-

sider it. The whole forest was a huge storehouse from which man drew indiscriminately whatever was best suited or most accessible for timber, for lumber, for charcoal, for tar. The settlers cleared millions of acres for agriculture by simply chopping down the trees and burning them where they lay.

It has remained for our own time, our own generation, the last few years in fact, to develop a *problem* of wood waste utilization and to make some progress toward its solution in a chemical way. In our day, ideas of conservation are prevalent and directing. The tar or charcoal burner of two or three hundred years ago in Russia or Sweden, and more recently in the Carolinas, centered his interest in the tar for his ropes or the charcoal for gunpowder or metallurgical purposes. To-day we approach the same manufacture with a view to utilizing waste materials. Here are certain residues unsuited for lumber, lath, railroad ties or box shooks, good only for fuel and unsalable at fair prices as fuel. What shall we do with them? Shall we or can we make tar or rosin, or alcohol or paper, or anything else that is marketable, and can we also secure a profit in doing so? The profit side is important because no matter how remarkable transformations are accomplished, or how interesting the process may be from a chemist's view point, still the law holds: no profit, no industry.

In this discussion we shall restrict ourselves mainly to this continent, mentioning only incidentally the work in Russia, Sweden, Austria Hungary, and other European countries. Our subject of wood waste naturally excludes most of the manufacture of paper pulp from spruce, poplar and hemlock, and some of the hardwood distillation, the extraction of tanning materials, dyestuffs, etc. In these excluded cases we are not specifically utilizing waste materials but are competing for the purchase of raw materials which are in some demand for other industries.

2. RAW MATERIALS

A list of the important woods of this Continent, which from their use for lumber would be a source of wood waste, would extend to more than a hundred names. For our purpose we may classify such as are of present interest as follows: *First*, the Longleaf Pine (*Pinus palustris*) in all the states touching the Atlantic Ocean or the Gulf of Mexico from North Carolina to Eastern Texas. This wood is exceedingly rich in resins and terpenes, and this tree makes the United States the largest producer of turpentine and rosin in the world. *Second*, the Shortleaf Pine (*Pinus echinata*) of the same distribution but extending farther inland, especially in Arkansas and Missouri, contains comparatively a small amount of resins and terpenes. The Loblolly (*Pinus taeda*) and the Cuban Pine (*Pinus Cubensis*) are intermediate between these two in their characteristics. These are the most important Southern pines. In the North, the Norway Pine (*Pinus resinosa*) occurs in Minnesota, Wisconsin, Michigan and the Province of Ontario. It does not occur in forests, but is scattered among other timber and in groves. A large portion of this has already been cut, and the waste for our purpose is in the form of stumps on uncleared lands. Like the Longleaf pine and other resinous trees these stumps do not rot. The bark soon falls away, the layer of sap wood decays, but the remainder apparently becomes more resinous with the years.

On the Pacific coast the Douglas fir (*Pseudotsuga Douglasii*) is especially abundant in British Columbia, Washington and Oregon. Individual trees vary considerably in character; some are rich in resins, particularly where it has collected in pockets or wind shakes; others contain very little. The amount being cut by lumber mills is very large, and any method of utilizing the waste either from mills or from stumps must recognize the variation and select the material suited for its purpose.

We next have the class of wood suitable for what is called hardwood distillation and including white pine, maple, oak, beech, birch, chestnut, ash and some other broad leaved woods.

¹ Paper presented before the New York Section of the Society of Chemical Industry, Chemists' Club, April 25, 1913.

These are the chief types having marked characteristics that have led to especial efforts for utilizing their waste.

Considering next the form of waste, the most immediate one is lumber mill refuse. It consists of the sawdust, the slabs, edgings and ends of the lumber. The sawdust and ends will have about the same average composition as the logs, but slabs and edgings contain a larger percentage of bark and sapwood. All the refuse is, of course, green and contains twenty-five to fifty per cent moisture. When cutting Longleaf pine that has been boxed for turpentine, many of the slabs are very resinous. *Second*, the limbs and tops left in the woods by lumbering operations: some of this can be gathered for hardwood distillation, but with the amount of other waste more available, the greater portion remains in the woods and soon decays or is burned. *Third*, the stumps: in resinous conifers these are the richest and most valuable for recovery of turpentine and rosin. Other stumps are too irregular and too expensive to utilize at present. A fourth form is the resinous "lightwood" from Longleaf pine trees which have died standing or have been blown down by winds. This has heretofore furnished a chief part of the coniferous wood used for distillation.

3. COMPONENTS OF WOOD WASTE

Disregarding the bark, we may consider all trees as composed of cells and ducts or interstices through which the sap flows. These cells are added in rings or layers externally, one ring for each year: a light colored part representing the spring growth and a darker colored part the summer growth. In conifers the colors are so sharply defined as to present two distinct rings, the summer growth here containing much more resin than the spring growth, and the percentage of summer wood decreases regularly from stump to top. In young trees the cells consist entirely of cellulose; in age they become encrusted with lignin or a ligno-cellulose ester. The sap is largely water. Green wood contains twenty-five to fifty per cent water, air-dried wood about twenty per cent, and wood dried at 150° carefully may be entirely freed of water. Such dried wood contains about 1 per cent mineral matter and the remaining cellulose and lignin contain about fifty per cent carbon, six per cent hydrogen and forty-four per cent oxygen. In addition, resinous conifers contain oleoresins, differing somewhat in each species. These are apparently simple mixtures of resin acids (rosin), volatile terpenes (turpentine), and in the case of lightwood, various higher boiling terpenes, terpene alcohols and esters (pine oil), probably formed from the terpenes by hydrolysis and oxidation. These pine oils occur in small quantities in green wood, but do not appear to any extent in the gum flowing from Longleaf pine trees when they are chipped for turpentine.

Water, cellulose, lignin, and the oleoresin which contains rosin, the terpenes and terpene derivatives, are the only constituents of any class of wood waste so far as we are concerned. Any other products derived from wood waste can come only by chemical transformation or decomposition of these constituents.

4. THE PRIMARY MARKETABLE PRODUCTS

(a) *Paper Pulp*.—We have mentioned cellulose, or at least the cellulose part of the lignocellulose complex as one component of wood waste. By removing the other constituents we can obtain cellulose, and wood waste then can be an important source of paper pulp. Hitherto it has not been. The raw materials for both chemical pulp and mechanical pulp or wood flour usually have been carefully selected and are comparatively high in price. This high price has caused diligent and successful search for other raw materials. Sapwoods of Shortleaf and Loblolly pines were commercially added to the list of pulp woods. The investigations, naturally extended to wood wastes, showed that most of them from Southern pines at least were capable of yielding merchantable paper pulp under proper treatment by the soda

or sulfate methods. The sulfito method is said to be less satisfactory.

It has still to be demonstrated whether the number of plants now projected will repeat in a commercial way the success that has attended the laboratory experiments in a chemical way. It is doubtless true that nearly any laboratory success or result that indicates financial profits can be repeated commercially; but the development of a laboratory process into a working plant paying dividends is a much harder task than is often realized, and many times requires years of united effort on the part of the best chemists, engineers, chemical engineers and business managers before it is accomplished. In this specific case, at least one plant has made pulp from waste wood, and transformed the pulp into very good grades of wrapping paper that have found a market. We are discussing the state of an industry and this one example brings paper pulp into our province. The advantages of waste wood for paper pulp are its cheapness and its quantity. The disadvantages are several. If made from mill waste the wood is green, full of water, has a large percentage of bark, and comes in irregular shapes. This means poor quality of pulp or large labor cost in selecting and greater manufacturing cost. If dead or fallen timber is used in conjunction with turpentine and rosin extraction by solvents, it will contain a large proportion of knots and charred wood unless carefully separated by hand. Shavings from a planing mill are comparatively free from all these disadvantages, and this has been used with success.

(b) *Ethyl Alcohol*.—Since wood waste contains cellulose, it must be regarded as a source of ethyl alcohol. The raw material used is bulky compared with the finished product and must be cheap in initial cost and have no labor charge for preparation or handling. This has so far restricted it to unselected mill waste from large lumber mills. Hydrolysis of the cellulose with very dilute acid produces glucose and fermentation of the glucose and distillation of the resulting mash gives a very satisfactory grade of ethyl alcohol. Some of the patents are over twenty years old. An unsuccessful plant was established in Mississippi nearly ten years ago. The processes are beautifully simple on paper, and in the laboratory, but it is only now that we can begin to say we have such a manufacture commercially. Years of experiment have been spent in determining the most favorable conditions of hydrolysis. The kind of acid, sulfuric, sulfurous, or hydrochloric, the per cent strength of acid and proportion to wood, the amount of water, the temperature, pressure, time, have all been found important factors in hydrolysis to obtain the maximum yield of fermentable sugars, and the minimum loss of those sugars by decomposition. Then problems of proper neutralization of the saccharine liquors and removal of extracted materials that prevent or retard fermentation; the development of special yeasts and fermentation methods for the liquors; the treatment of residues to furnish suitable fuel for the plant. All these problems have now received solutions adequate enough to furnish a total production of 5,000 to 10,000 gallons ethyl alcohol per day from wood waste in two plants, one in South Carolina and one in Louisiana, both working on mill waste from Southern pines. The field is an interesting one, and in view of its possibilities should be attractive to investigators.

(c) *Acetate of Lime, Wood Alcohol and Charcoal*.—When wood is heated somewhat above 200° decomposition begins. Water distills first, then dilute acids, mainly acetic. At about 275° considerable wood alcohol is in the distillate, and light tar oils and gas are flowing freely; at a higher temperature heavy tar oil flows, and finally only charcoal is left in the retort. With uniform and careful heating 350° produces good charcoal and 300° brown charcoal, although observed temperatures on retorts are usually higher owing to unsatisfactory heat distribution and transmission. The reaction is exothermic and above

280° with proper insulation, will support itself. Cellulose distilled alone gives no methyl alcohol, but otherwise the phenomena are the same. We must look to the lignin part of the wood for the methoxy groups furnishing methyl alcohol. No matter what wood is distilled there will be the same products, varying, however, in quantity with the kind and dryness of wood and with the rapidity of heating or speed of removing products from the retort during distillation.

The manufacture of acetate of lime, wood alcohol and charcoal has not been essentially a wood waste utilization industry. Individual plants often take a part of their wood in the form of slabs from adjacent hardwood sawmills; one small plant recently started operating in Tennessee on oak slabs, but commercial figures are not yet available. In the main, plants have been established not primarily to use waste material, but to supply a demand for charcoal in nearby blast furnaces. Slabs are, of course, cheaper than cordwood, but the yields obtained from them are somewhat smaller, and a belief has existed in many quarters that they could not be satisfactorily distilled alone. The yields from good air-dried hardwood are, of charcoal 30 per cent, or a little less, wood alcohol 10 gallons per cord, 82 per cent gray acetate of lime 200 lbs. Pine woods give much smaller yields, the type usually distilled in the South, for example, producing only about 20 per cent charcoal, one to two gallons methyl alcohol per cord, and 50 to 75 pounds acetate of lime, either brown or much more difficult to refine than the product from hardwood. Recovery of these smaller amounts of alcohol and acetate has been attempted in a commercial way, but is now entirely abandoned. Charcoal from pine wood usually commands a ready sale for household or manufacturing fuel, if the plant is favorably located.

(d) *Turpentine, Pine Oil and Rosin*.—Coniferous woods in general, and the Longleaf pine, Norway pine and Douglas fir in particular, contain oleoresins. These are partly physiological and mainly pathological secretions of the resin ducts, and are not to be confounded with the sap of the tree. When a coniferous tree is wounded a secretion flows from the wound. In the case of the Longleaf pine, the wound must be re-opened by chipping at least every week to keep the gum flowing. Since the oleoresin is so largely a pathological product, the more the tree is wounded and the larger amount of oleoresins we take from it, in this manner, the more remains or is formed in the body of the tree, and the richer we find it when we work it up as waste wood. This oleoresin may be completely separated by chipping the wood and extracting thoroughly with a solvent. Fractional distillation of the extract, usually in the presence of steam, separates it into solvent, turpentine, pine oil and rosin. These are the only products directly obtainable from the oleoresin, and none of these is obtainable from any other portion of the wood excepting the oleoresin. Of course, it is not necessary to isolate the oleoresin. Direct heating of the wood will drive off the turpentine and pine oil, and if the heating is continued, will melt out part of the rosin, decompose the rest of it, and mix rosin naphtha or rosin spirit with the turpentine.

Simple steam distillation of the wood will remove most of the turpentine and pine oil alone. However these products are extracted, they will be slightly different from the turpentine and rosin obtained by chipping the tree. The turpentine is liable to be contaminated with the products of distillation of the rosin, or of the wood, or of the bath, or of the solvent used in its preparation. If considerable heat or pressure has been used, particularly in the presence of acids either already in the wood or derived from its decomposition, partial transformation of the pinene to dipentene occurs. Methods of refining have now progressed so far, however, that where proper care is used in manufacture, a very satisfactory and uniform turpentine is marketed. It has a slightly different odor from gum turpen-

tine, and even the best of it in a commercial way does not quite meet the specifications as to the amount distilling between certain limits, as does gum turpentine. This is apparently due to a slightly larger content of dipentene or *B* pinene or both. This difference in proportion of constituents makes a slight difference in its solvent power. When properly made and refined, it finds widely extended use wherever gum turpentine can be used. So far as I know, it contains no constituents that are not present in ordinary gum spirit of turpentine.

The rosin extracted from wood has usually been of about an E grade, so far as color is concerned, but has been somewhat softer than the corresponding grades of gum rosin. This is due to a certain amount of heavy oils, about one per cent, which still remains in the rosin extracted from wood. This remaining one per cent of oil can be removed under proper conditions, and when this is done the rosin extracted from wood is not in any respect commercially different from the gum rosin. Most of the plants up to the present, however, have not removed this last fraction of heavy oil, and have been content to market their rosin in industries where the oil content would not interfere with its use.

Pine oil is a mixture of terpene alcohols, esters, ketones, and other derivatives boiling mainly between 210° and 225°. The ordinary product has a gravity of about 0.940, although special products are put out of either higher or lower gravity. Its chief constituent is terpineol. About twenty different terpene derivatives in all have been isolated from it. It finds quite an extended use as a solvent, and also as a raw material for manufacturing or isolating various terpene products.

(e) *Tar, Tar Oils, Creosote Oils, Pitch, Light Oils, Wood Oils, Gas*.—Whenever cellulose, lignocellulose, or any variety of wood is distilled, we obtain gas, tar, and light oils. In the case of hard woods, the gas and tar are used entirely for fuel to aid in the distillation. Tar from hard wood has not so far been worked up into marketable products, with the exception of some of the light distillates of the tar known as wood oils, which have found a limited market in manufacturing shingle stains and similar products. When we distil a resinous wood, the decomposition products of the rosin are mixed with those of the wood. In this case the tar becomes naturally much more valuable. It finds a ready market as such, particularly in the rope-making industry, or it may be distilled and refined to produce tar oils, which find a limited market, particularly in the drug trade, creosote oils, which find a very fair market in special industries, and which should be largely used in preserving timbers, if the price of coal tar preservative continues to rise.

The light oils from resinous woods, which are between tar oil and turpentine in their character, find a very limited market.

The residue from distilling tar is pitch. You find this same residue in distilling rosin, and of course in distilling wood where the temperature inside the retort is properly controlled. Pitch is readily marketed both in this country and abroad.

These are the main primary products produced from wood utilization plants. It is obvious that no one plant can produce them all. If, for example, the rosin is extracted and sold as rosin, there will be no production of marketable tar and pitch.

(f) *Cattle Foods*.—We have noticed that the cellulose of wood and possibly part of the lignin can be hydrolyzed rather easily to form glucose. There are, of course, a number of other sugars formed, the total from pine wood being about 23 per cent; from hard wood, possibly 26 per cent or more of the dry weight of the wood. In addition, there are other soluble carbohydrates and considerable quantities of unchanged cellulose and the lignin part of the molecule. A large part of the soluble carbohydrates are presumably thoroughly digestible, and as cattle are able to digest certain varieties of cellulose, it is possible that a certain percentage of the insoluble portion may be digestible. When this digested wood is mixed with cane syrup, peanut

meal, rice meal, alfalfa, etc., it seems to make good cattle food and finds a market.

5. THE SECONDARY PRODUCTS

(a) *Acetic Acid and Acetone*.—Nearly all of the acetic acid and a very large part of the vinegar in this country is produced directly from acetate of lime by treatment usually with sulfuric acid and more rarely with hydrochloric acid. The acetate of lime is usually shipped from the point of manufacture to separate chemical plants for its further conversion. The manufacture of acetone in the same way is entirely dependent on the wood utilization industry. It is made exclusively by direct distillation of acetate of lime. This being the source of acetone, it follows that indirectly the manufacture of chloroform and iodoform are dependent on the same industry.

(b) *Camphor*.—A number of processes lead from pinene, the chief constituent of turpentine, to camphor, and some of these at times have been placed on a commercial basis. When turpentine was fifty cents per gallon and camphor one dollar per pound, this was a profitable industry. When turpentine went to one dollar per gallon and camphor to fifty cents per pound, it was an unprofitable one. To-day, so far as I know, camphor is not being made synthetically. Whenever there is a rise in the price of camphor, or a decided improvement in the yields of camphor obtained, there is no reason why it should not again become an industry. On the other hand, if the use of camphor should decrease, due possibly to a more extended use of other materials in place of celluloid, it might never be a profitable industry again, even with low-priced turpentine and good yields.

(c) *Rosin Oils*.—When rosin is heated in the neighborhood of 300°, or a little less, a steady and uniform decomposition occurs, giving water and light rosin spirits, and afterwards rosin oils. Some of these oils find extended use in the manufacture of axle grease and other lubricants, others in making printing ink. The pitch residue remaining in the still has already been mentioned. Rosin extracted from waste wood gives the same products, but unless the heavy oil mentioned above has been entirely removed from the rosin, the oils have rather a sharp odor, which must be removed before they can be used, for example, in printing inks.

A good many attempts have been made to devise a process by which resinous wood could be converted into paper pulp by the soda method, and the soda liquors which contain rosin distilled directly for the production of rosin oils. This can be done, and has been done in a small way, but the rosin oils obtained differ from the ordinary commercial product, being lighter in gravity and more mobile, and the process is not to-day a commercial success. In no case at present are rosin oils being manufactured in the primary wood utilization plants.

(d) *Wood Preservative and Paints, Disinfectants, Sheep Dip*.—Tar is often a source of delight to the organic chemist, because it is so full of possibilities, but it is always a source of discouragement because of the difficulty of realizing those possibilities. Tar and its various distillates contain considerable amounts of cresols and their derivatives. It is fairly easy to obtain distillates which have good properties as wood preservatives, either for impregnation or, when mixed with pigments, for external application. It is also fairly easy to obtain distillates having about the consistency of linseed oil and which may be of value in certain external paints when substituted for the linseed oil in the paint. In either way, there is here a valuable source of wood-preserving material, and it has been utilized, although in a very small way, for a great many years, particularly in railway equipment. This same occurrence of cresol has led to a great variety of disinfectants for stables, for lavatories, for sheep dip, etc. Pyroligneous acid obtained from resinous wood is chiefly water, but it contains small amounts of acetic and formic acids, wood alcohol, acetone and cresol.

This has led to its limited use as a preservative and also as a general disinfectant for stables, and for refuse generally. All of these, no doubt, have values, but up to the present there has been no uniformity in their manufacture or composition, and no particular volume in the amount of business. It is a promising field rather than a present industry.

(e) *Perfumes, Liniments*.—Pine oil has been shown to contain terpineol, cineol, fenchyl alcohol, camphor, borneol, methyl chavicol, and a variety of other terpene derivatives. It contains nearly 50 per cent. of terpineol, and as terpineol is used extensively in the perfume industry, pine oil has come to form one of the commercial sources of that product. Most of the constituents of pine oil also have mild antiseptic and local anaesthetic properties, and all products of the pine have always enjoyed a high reputation in cases of lung troubles. This has led to a large and increasing consumption of pine oil in the drug trade, and among the manufacturers of patent medicines.

(f) *Embalming Fluid and Specialties*.—So long as products have not been thoroughly investigated they contain wonderful possibilities, and a great many plants on a basis of slight investigation have put out long lines of special products covering almost the whole range of human requirements, living and dead. These are so variable and there is such a lack of uniformity and precision in different cases that it seems useless to go into them in detail, particularly since we can hardly dignify it by the name of an industry as yet.

When turpentine or pine oil is distilled with steam, as is ordinarily the case in wood utilization plants, the condensed water holds a certain amount of terpene constituents in solution, and this condensed water has often been found of value as a mild antiseptic, and has been the basis also of the manufacture of embalming fluid.

6. THE VARIOUS PROCESSES

(a) *Hardwood*.—Originally wood was distilled in heaps covered with turf, a portion of the wood being burned to carbonize the rest. This was improved by substituting permanent kilns, usually of brick, for the turf. Where charcoal is the chief product required, these are still in extensive use. More than half the acetate of lime and wood alcohol are lost, however, if their recovery is attempted at all from kilns.

Three methods of distillation are at present used in this country, in addition to kilns: *First*, a vertical retort, the wood being placed in a basket, lowered into the retort and the charcoal removed in the same way after distillation. The retorts are quite small, and I have seen them only in New England. *Second*, the horizontal retort holding nearly a cord, and usually set in pairs. These are used largely in New York and Southern Pennsylvania. *Third*, the large, horizontal steel ovens approximately 60 feet long, where the wood is run in on cars and the charcoal is withdrawn soon after distillation is completed, and allowed to stand in coolers until it can be brought safely into the air. This type of plant is used largely in Michigan, and is the most efficient one now operating. The yields average about ten gallons wood alcohol, 200 pounds acetate of lime and 50 bushels charcoal per cord of wood. Gas and tar are used as fuel for the retorts, there being very slight encouragement at present to utilize any of the tar or its distillates. Hardwood distillation has been repeatedly described in the literature, and further discussion here would not be profitable.

(b) *Paper Pulp*.—So far as I know, only one plant is to-day manufacturing paper pulp on a commercial scale from what would be called wood waste. This plant started operation on planer shavings by the sulfate process. Some attempt has been made to recover turpentine and pine oil. A yield of forty or fifty per cent, computed on the dry wood, would be expected, and the paper made from the pulp so far has been chiefly a good grade of wrapping paper. A great many experiments are at present under way and a number of plants are projected, but to-day

we must say that the industry has a future rather than a history.

(c) *Ethyl Alcohol.* In the two plants operating to-day, the material is Shortleaf or Loblolly pine unselected waste from lumber mills. All the waste is ground and shredded, then treated in large rotating digesters with very dilute sulfuric acid at high pressure and high temperature for a short time. The digested mass is then extracted in diffusion batteries, the extract purified and taken to the fermentation vats and the residue pressed to remove a part of the moisture, and sent to the boilers. After the fermentation the liquors are distilled as usual to produce 95 per cent ethyl alcohol. The yield may be considered to be about twenty gallons per ton of material. This can, no doubt, be increased with improvements which would prevent decomposition of sugar during digestion and which will increase the percentage of fermentation in the presence of the large amounts of other extractive, unfermentable materials.

(d) *Destructive Distillation.*—Of course hardwood distillation is destructive distillation. This present section refers to distillation of resinous woods. This has been conducted on the three chief varieties of resinous woods: Longleaf pine in the South, Norway pine in Michigan, Wisconsin and Minnesota, and Douglas fir on the Western coast. There are, and have been, a very large number of such plants operating with a great variety of retorts and kilns. By far the greater percentage have been unfortunate financially. A few have been operating continuously for years. The most important improvements in recent years have been in simplification of the process, reduction of labor costs, and more accurate control of the temperature. Only rich resinous lightwood or stumps or sawmill slabs which are rich from having been chipped for turpentine, can be used profitably. Yields vary with the wood and with the plant. A fair estimate would be ten gallons turpentine, one to two gallons pine oil, one to two gallons very light oils containing most of the rosin spirits, fifty gallons tar, one hundred pounds pitch, forty bushels charcoal per cord. Of course these same products are often converted into other materials before they are marketed, but the figures given represent a fair estimate of what is obtained in a good plant. If the raw material is not too expensive, the plant well managed, the material properly prepared for the market, and the shipping facilities good, there is a margin of profit. The margin is not large enough, however, so that any of the above precautions can be neglected.

(e) *Steam Distillation.*—When turpentine was seventy-five cents or more per gallon, the process of steam distillation alone was a real industry. To-day it is a part of history excepting in the case of two or three plants working on sawmill waste. In these cases where the sawmill waste costs nothing, the wood is chipped, extracted for a very short time with steam in retorts of which a great variety has been in use, and the extracted wood immediately conveyed to the power house. By a proper system of conveying and retorts, the cost of handling is very low. The cost of raw material may be considered as almost nothing, and the yield of a gallon or two of turpentine per cord and a little pine oil will show a profit on the investment.

Steam distillation plants for extracting lightwood in the same manner were quite common two or three years ago, but not one is now operating. It should be said in their favor that they were the first ones to produce good marketable turpentine extracted from wood, nearly approximating the gum turpentine, and they should further be credited in most cases with establishing their plants under the proper assumption that they were installing only a partial process which must be completed by the further extraction of rosin or other products before they could hope to be on a sound foundation. This, in a measure, is being realized in some of the solvent plants where turpentine and pine oil are recovered by regular steam distillation methods before the rosin is extracted. The same thing has been done

in a small way with the paper pulp plants and the ethyl alcohol plants.

(f) *Bath Processes.* Two plants are now operating and have been for some years on what is called the bath process. In this system the wood is placed on cars and run into a retort and the retort is then flooded with a hot bath of high boiling material. This bath extracts the turpentine and pine oil and probably some of the rosin from the wood, and by driving steam through it the turpentine and pine oil are recovered, and the bath may be used over again. The bath may be made of rosin or of mixtures of rosin, pitch, tar, etc. After the wood has been extracted in this manner, such parts as are not needed for fuel are conveyed directly to destructive distillation ovens and distilled in the usual manner.

(g) *Solvent Processes.*—Rosin is soluble in carbon bisulfide, carbon tetrachloride, alcohol, turpentine, gasoline, naphtha, etc. The chief solvent used in extracting so far has been mainly a grade of naphtha, the initial boiling point being not usually lower than 85°, and all distilling below 120° or 140°. The wood, ordinarily lightwood or stumps, is chipped in an edging grinder, shredded, and placed in a retort. In some cases the turpentine and pine oil are then steamed off and the solvent added, while in other cases the solvent is added in the beginning. The former process requires more time and as it leaves the wood moist the succeeding extraction with solvent is supposed to be less efficient than in the latter case. On the other hand, if the solvent is added initially, the turpentine and pine oil become mixed with it, and a complete separation so that the turpentine contains none of the solvent is very difficult and in some cases commercially impossible. The solution containing rosin is concentrated, and finally the last of the oil is driven off with steam or superheated steam, leaving the rosin in good condition to market. Ordinary lightwood may be said to yield ten or twelve gallons of turpentine, two or three gallons pine oil, and four hundred to four hundred and fifty pounds of rosin per cord. Stumps will yield from six hundred to six hundred and fifty pounds of rosin, and proportionately larger amounts of turpentine and pine oil. Norway pine stumps usually yield about three hundred pounds of rosin.

There are at present at least eight plants in this country either operating or ready to operate by the solvent process, situated in Mississippi, Alabama, Florida, South Carolina and Michigan. The apparent difficulty is the loss of solvent amounting ordinarily to twenty or twenty-five gallons per cord extracted, and as the solvent used in most cases has increased very rapidly in price in the last two or three years, and is still increasing, this fixed cost becomes a very heavy charge on the plant.

(h) *Cattle Food.*—This is allied to the ethyl alcohol production, but it stops with the hydrolysis of the cellulose. It has been in operation in England for two or three years, and a small plant has been operating in this country in Wisconsin for about a year. The hydrolyzing agent is sulfur dioxide and the conversion of material such as wood waste into food certainly looks promising.

7. THE PRESENT SITUATION AND TENDENCY

In hardwood distillation the tendency is to the continued use of the large oven with cars like those used in Michigan. Improvements have been limited mainly to small ones giving slight increase in yield, and more attention has been devoted to simplifying processes of separating and purifying wood alcohol and acetate of lime. There is no rapid increase in this industry. The paper pulp production seems to be only in its infancy. There has been too much tendency to regard the manufacture of turpentine and rosin as the main operation of a plant with paper pulp as a by-product. This must be entirely reversed, and plants must be built where necessary particularly designed for the manufacture of paper pulp and the material must be selected for that purpose, and turpentine and rosin, where re-

covered, must be considered as by-products. The manufactures of ethyl alcohol and of cattle food must also be regarded as still in their early stages. The processes are similar in the first stage but of course are mutually exclusive. If the material is used for cattle food it cannot be fermented to produce alcohol, and *vice versa*.

In destructive distillation plants working on resinous woods, the tendency has all been in recent years to careful control of temperatures, simplification of process, and selection of wood. In this field more than in any other there is an opportunity for careful examination of the products and development of their use for special purposes. The only excuse for destructive distillation is the small cost of the plant and cheapness of operation. Aside from this it is much more rational to separate the oleoresins from the lignocellulose and treat each one in whatever way seems desirable. The number of destructive distillation plants does not seem to be increasing with any particular rapidity, but the ones that are firmly established seem to bring in fair returns from their operation.

Steam distillation alone as a method of treating wood is dead, excepting where the plant works on mill waste exclusively. If a mill is cutting Longleaf pine, particularly timber that has been boxed, this forms a cheap and efficient installation and pays interest on the investment.

The bath process plants with succeeding destructive distillation of the wood have neither increased nor decreased in number recently.

Solvent process plants have increased very rapidly within the last year or two, but with lower prices of turpentine and rosin, and higher prices of solvent they are beginning to see difficulties ahead, and may find it necessary to change the character of solvent, or change the method of extraction.

Many schemes are floating in people's minds of combining various processes into one, for example, a combination of steam distillation solvent process and paper pulp, but these are still in the future. There is at present a very healthy interest in conservation in general, and in the utilization of wood waste in particular. It is a field that produces remarkable enthusiasm in the investigator, and if this interest and enthusiasm are controlled by a sane consideration of the difficulties in each particular case, a dispassionate review of former lack of success in similar or allied cases, and a willingness to learn from previous experience, there is no reason why the present tremendous waste in this field should not be converted into a large annual income.

50 EAST 41ST STREET, NEW YORK

THE RELATION OF THE MANUFACTURER TO OUR PATENT SYSTEM¹

By W. M. GROSVENOR

Carlyle has well said, "Did we imagine that much information or any deep sagacity were required—it would ill become us to step forward on this occasion. But surely it is given to every man if he will but take heed, to know so much as whether or not he *knows*. Let the reader be patient with us then; and according as he finds that we speak honestly and earnestly, consider our statement."

About a year ago a statistical paper² was read before a joint meeting of chemical societies on "Patents and the Chemical Industry in the United States." At the time this was not seriously discussed or commented upon by your Patent Committee because the paper represented so much work that it seemed a pity to sharply criticize conclusions modestly offered. But the paper seems to have been read by many people lacking in practical comparative and critical faculties, and the astonishing conclusions it offers appear to have been swallowed whole by

¹ Presented at the Boston Meeting of the Am. Inst. Chem. Eng., June 25-28, 1913.

² Herstein, *This Journal*, 4, 328.

so many unthinking readers that a careful criticism of the paper is demanded.

The statistics were prefaced with the statement that "*The close interrelation between patents and the development of modern industry is a subject receiving sufficient consideration on the part of economists.*" This is unfortunately not true in the United States. In Germany the Government is revising the Patent Laws, making them in most respects more like our own. In this work the suggestion and the cooperation of manufacturers, engineers, agents, corporation lawyers and patent attorneys is sought. Such a method is far more promising of practical benefit than the "consideration" of our "economists," some of whom would hardly know a patent if they saw one, and a majority of whom apparently regard public hearings as mere formalities to be ignored in actual procedure. In this country we haven't even the sufficient attention of the "economists" unless the patent commissioner and the politician who get together for mutual benefit at the expense of the Patent System can be called in certain senses economists. They may be entirely sincere in their motives but the "reforms" they have advocated are so plainly in the interest of the "Trusts" that we must either believe them influenced or question their intelligence.

The author of that paper recognized the strong tendency on the part of inventors to distrust the protection of patents and stated that already inventors prefer to keep improvements secret rather than patent them. He admitted that even with the right of patenting the product (if new) this secrecy is "only partially overcome," but he does not frankly state the actual reason. He either does not know, or else ignores it entirely because it would disagree with the trend of his comments and conclusions. Those who have to recommend or decide what shall be done in these cases realize that it is because the right in intellectual property is too insecurely granted by the U. S. patent; because the grant is only a contingent liability, a right to sue; because our "priority of conception" doctrine with its interference proceedings, helps to make the title to any invention problematical even after a patent grant; because searches, often slovenly, are made through a woefully incomplete and partly unclassified record of the prior art, in part at least by underpaid assistants waiting to pass their law exams and find another job; because the absence of public opposition or expert advice from practical men makes those searches academic; and because by every technical complication from the drawing of our claims as permutations of hair splitting, through the multiplicity of appeals to our court practice as it has been (rules of procedure) and to some extent still is (9 circuits with untrained judges and contradictory decisions), the great advantage is given at every step to mere money power. If real estate titles were subject to all these risks, liabilities and uncertainties, who would care to buy a home? Why should brain property be thus jeopardized!

So when we were informed that "*as a whole the progress of industrial chemistry in recent years is recorded in patent literature*" it is because the paper was written by a statistician not himself a practical, technical chemist. It would be surprising if true. Actually progress is barely indicated, as incompletely as the law permits, only for those things that can't be kept secret and only after it becomes necessary to issue the application in order to defend as best we may rights that are being overrun.

Let us proceed to the statistics¹—a magnificent piece of statistical work—which it is stated "*should not by any means be regarded as including those patents relating to chemical industry which are classified under other divisions or sub-divisions*" in other words, many of the most important truly chemical patents, separately classified because most important.

It was then pointed out as an awful condition of things that the number of chemical patents issued to German citizens (1754) is greater than that issued to U. S. citizens (1552), that German

¹ Omitted here to save space. See *This Journal*, 4, 329.

percentage claims 70 to our 19 of the patents for carbon dyes, 70 to our 31 on dyeing processes and 450 to our 130 on carbon compounds. Did these figures really tell the story of chemical industry as the paper endeavored to show, how terrible the tale would appear to be. But the practical man is apt to ask, "Well, what do they mean? What is it all worth?"

In the first place we note from the figures themselves that 1754 patents were issued to Germans for all chemical inventions and 1246 (or 70 per cent) for these three groups (carbon dyes, carbon compounds and bleaching and dyeing). Do these three little groups constitute, as would thus appear, over 70 per cent of all chemical industry? We seem to see a light.

In the next place, the grand total value of carbon dyes imported to the U. S. last year approximated \$9,000,000, and the total of all products of this class \$81,000,000. We import over \$10,000,000 worth of dolls and New York eats \$25,000,000 worth of eggs. Is it possible that 81 million is 70 per cent of all the products of what we call "chemical industries?" The whole carbon dye business is about the size of our little aluminum business started at Niagara Falls under an American patent. Also the total \$81,000,000 is about the same as the value of sulfite and caustic pulp made last year, another American invention. We even made ourselves in the U. S., \$16,000,000 worth of drugs and extracts, not counting patent medicines. In the 1900 census, over 200 millions worth of chemical products are recorded as such, not including the separately classified industries. Furthermore, simple division shows each of these terrible German patents to represent a total gross business in the U. S. of about \$70,000 a year. Let us compare this with some American inventions. Last year we made about 90 millions of wood pulp and we vulcanized about 93 million dollars worth of rubber, made 10 millions of aluminum above indicated, 6 millions photographic materials, 3 millions of pyroxyline plastics, 6 million dollars worth of oxide matches, 3 million dollars worth of calcium carbide, and nobody knows just how much nickel steel, with carborundum, alundum, Acheson graphite, bakelite, etc., climbing up to join the procession. Instances of real chemical products in quantities many times \$10,000 a year, made under patents of U. S. inventors, could be multiplied almost indefinitely.

Let us even take the statistician's standard for measuring progress as indicated by number of patents and look at the relative progress of Germany and the U. S. in other lines (some more important than dyes) that this table (admittedly limited) covers. We find alkalies and chlorine 70 to 4, bleaching and disinfecting 20 to 12, chlorates 7 to 1, dyes and pigments 19 to 0, carbides 58 to 3, tanning 5 to 0, bleaching 30 to 17, dyes (not carbon) 16 to 10, mercerizing 29 to 10, mordants 21 to 13, mineral acids 116 to 62, fire extinguishing compounds 5 to 4, catalytic bodies 5 to 10, metalloids 55 to 14, packing chemicals 10 to 2, apparatus 40 to 10, salines 146 to 98, ammonia 6 to 27, soda and potash 24 to 9, nitro compounds 97 to 28, extracts 44 to 18, internal remedies 23 to 52, tropical remedies 45 to 20, insecticides 69 to 6, disinfectants 240 to 19, pyroxalines 20 to 10, viscose and cellulose 17 to 28, plastics 12 to 0, glue 12 to 8. In each of the 9 divisions of coating compositions we exceed totalling 80 to 20, as also in ammonia, water, and wood distillation total 35 to 7. There are not many italicized branches in which Germany seems to take more patents. And consider the relative commercial importance of alkalies and chlorine 15 million, carbides 4, mineral acids 20, tanning 204, bleaching 3, salines 10, soda and potash 18, nitro compounds 16, internal remedies 23, pyroxyline plastics 3, or glue 6, along with fertilizers 50, copper smelting 165, lead smelting 175, glucose 21, paints 50, soap and candles 53 and sugar 250 million as compared with coal tar dyes 9 or the whole 81 million about which so much noise is made.

And yet what awful "conclusions" this little bunch of German

dyes produced in the paper and what horrible things we are advised to do to our patent system and chemical industries producing over 1000 million a year because 80 millions worth of German chemicals are imported or rather because 1151 patents are granted to Germans. Suppose I say that they paid our Patent Office \$26,775 and paid our attorneys about \$115,000 and therefore urge the importance of retaining the present law as it is. This would be about as sane as for any one to call "dyes" and "carbon compounds" the chemical industry and seek on account of these relatively unimportant groups to perform criminal malpractice on our whole patent system. Why that paper would have us abolish the "product patent" and introduce compulsory working for a matter of about 80 million dollars worth of imported products a year!

Statistics are, as we have seen, valuable and instructive but the conclusion drawn and recommendations made in this paper are outrageous, contradictory of the common sense interpretation of the very figures on which they are supposed to be based and flatly contradicted by more complete facts in the specific case. For instance, "In the United States the progress of chemical industry must be traced not by the broadening of domestic production but in imports only." It seems incredible that with any study of the field a writer should have made this statement. Let us have a few real industrial statistics. [In the selection of the statistics of industries, I wish to thank Mr. O. C. Hagemann for generous assistance.]

The latest census figures show the value of all products of the United States chemical industries to have risen from \$757,127,000 in 1900 to \$1,479,000 in 1910; doubled in ten years.

Included are lubricating oils, baking powder, blacking, blues, printing ink, candles, pharmaceutical preparations, tanning and dyeing extracts, paints, colors, artificial manures, glues, fats and oils, inks, pigments, perfumes, refined mineral oils, soap, starch, turpentine, resins, varnishes, products of destructive distillation and chemicals in the narrower sense.

The production of these chemicals in the narrow sense has grown from \$62,637,000 in 1900 to \$117,689,000 in 1910, an increase of \$55,052,000 or 88 per cent.

IMPORTED COAL TAR CHEMICALS AND OTHER SUBSTANCES (a)

		Year ending June 30th, 1912	
Include	Acid, carbolic.....	\$	521,457
	Alizarine.....		1,386,529
	Aniline oils.....		175,120
	Aniline salts.....		386,656
	Other coal tar chemicals.....		10,755,160
			\$13,224,922
		Year ending June 30th, 1912	
Forward.....			\$13,224,922
Exclude	Balsams.....	\$	138,000
	Barks, beans, etc.....		2,391,606
	Ergot.....		187,000
	Flowers and leaves.....		704,547
	Gums.....		10,480,396
	Jalap.....		27,607
	Nutgalls.....		329,457
	Opium.....		2,020,026
	Potash muriate.....		7,235,728
	Roots.....		1,688,865
	Saffron.....		90,202
	Soda nitrate (Chile).....		15,427,904
	Tonka beans.....		201,131
	Vanilla beans.....		2,025,153
	Wax, vegetable.....		1,080,198
			\$44,027,820
			\$57,252,742
Total chemicals, drugs, dyes—imported in 1911-12			\$90,878,000
Deduction as above.....			44,027,820
Remnant.....			\$46,850,180

(a) Some of these should be excluded from the imports when comparing United States productions with imports of chemical manufactures.

The imports of "chemicals" amounted to \$37,559,000 in 1900 and \$63,388,000 in 1910, an increase of \$25,829,000, or 69 per cent.

If from the imports of all "chemicals," drugs and dyes, \$90,878,000 we should strike out Chile saltpeter, German crude potash salts and natural raw materials like leaves, bark, etc., = \$44,027,000, the chemical, dye and drug imports that we might manufacture remain a modest total of \$46,850,000.

This remnant amounts to not more than 40 per cent of our present home produce of strictly chemical preparations and less than 4 per cent of products of our really chemical industries.

In examining detailed items we find:

RAPID PROGRESS IN MANUFACTURING AND THE MORE STATIONARY CONDITION AND DECLINE OF IMPORTS IN THOUSANDS OF DOLLARS

	PRODUCTION				Imports			1910
							Imp.	
	1900	1905	1910	1900	1905	1910	Prod Per cent	
Acetic acid	396	538	1136	18.00	16.00	82.00	7.2	
Alum and alum cake			2580	19.00	23.00	31.00	12.0	
Boric acid.	198	527	296	17.00	23.00	13.00	4.4	
Borax.	502	2123	1767	2.00	13.00	1.00	0.1	
Chlorates.			940	195.00	146.00	266.00	28.3	
Chloride of lime (bleach)			1507	1461.00	776.00	750.00	49.7	
Chloroform.	58	166	473	0.3	0.29	1.4	0.3	
Citric acid.		599	777	14.0	0.72	9.0	1.1	
Epsom salts.	46	146	358	2.0	31.0	27.0	7.5	
Glycerine.	2013	5348	11728	21.2900	2050.00	3674.00	31.3	
Phosphoric acid.		68	506	21.00	26.00	47.00	9.4	
Potassium cyanide.	591	496	1478	444.00	260.00	328.00	22.2	
Prussiate yellow.	994	683	464	224.00	103.00	229.00	49.5	
Soda ash.	4768	8202	10362	665.00	167.00	55.00	0.6	
Sodium bicarbonate.	1325	1136	1515	4.00	6.00	4.00	0.3	
Soda caustic.	2918	2924	5216	158.00	35.00	33.00	0.6	
Sodium phosphate.	105	244	500	43.00	1.00	1.00	0.2	
Sulfuric ether	130	335	199	0.03	0.16	0.07	0.1	
Zinc salts			1478	37.00	31.00	36.00	24.4	

To which may be added a list showing our development in some cases not directly comparable with imports because the latter are not separately listed:

PRODUCTION	Values in \$1,000		
	1900	1905	1910
Acetone	178	161	703
Alkaloids	1,743	2,926	3,188
Ammonia sulfate.....	331	681	3,227
Anhydrous ammonia	448	1,173	2,503
Anhydrous carbonic acid.....	696	1,344	2,318
Bleaching materials aside from hypochlorites.....	492	778	1,635
Calcium carbide	680		2,984
Fine chemicals, aside from alkaloids, salts, of gold, silver and platinum, chloroform, ether, acetone	1,426	4,249	5,200
First distillation products from coal tar.....	800	341	2,462
Hydrofluoric acid.....	35	151	215
Mixed acids	1,111		1,860
Muriatic acid.....	1,020		1,171
Nitric acid.....	1,455		1,357
Plastic masses	2,099	4,756	7,180
Sulfuric acid.....	7,679		10,084
Tin salts.....	470	905	1,195

In view of the facts, any statement that growth is shown by imports only would be humorous were it not that many are deceived.

The author of that paper offers "..... to point out anew those characteristics of our patent legislation which, in their bearing on chemical industry at least, are calculated to retard rather than to promote the development of manufactures in the United States." We have seen how retarded is chemical industry broadly. If in some small section (as carbon compounds or dyes) we find the contrary, it must be charged to neglect by our manufacturers or their false economy of chemical research, or some other cause peculiar to that specific line, not the patent law or the tariff

that equally affect lines where we have seen such phenomenal growth of production.

"Chemical manufactures are but a small, even if a very important, part of our industrial structure." The last general census showed about 13 thousand million total manufactures of which 1400 million (11 per cent) were chemical and allied industries and the strictly chemical classification exceeded 117 million. So we are forced to conclude that dyes and carbon compounds are all the author considers as chemical manufactures, or that he has some special interest to serve in ignoring "the other ninety and nine."

"Expressed in number of patents taken out, the figures quoted before show that scarcely more than one per cent of patents issued cover invention properly (arbitrarily?) called chemical." How properly and how arbitrarily we have seen.

"No one at all acquainted with the subject will deny, and a study of the foreign trade statistics will immediately show, that the building up of chemical industry in this country has been extremely one sided. I have a remote bowing acquaintance with the subject and emphatically deny the statement. Furthermore, trade statistics do not show it, as you have seen, unless mere number of paper patents are "trade statistics." In fact, it is denied in the next sentence though the author didn't know it. He says: "The manufacture of heavy chemicals on the one hand is in most respects on an equality with the best anywhere and the same is true of staple, organic and medicinal chemicals." Any one of these three is comparable with the organic dyes' 9 million and he ignores wood distillation products 4 million, pyroxylin and similar plastics 7, glycerin 12, our own dyestuffs and extracts 15, electrochemicals 18, turpentine and rosin 25, explosives 40, glucose and starch 48, fertilizers 104, soap 111, paints and varnishes 124, cottonseed oil and cake 147, gas and by-products 167, petroleum products 237 and refining of metals over 300 million and numerous other branches of industry which are strictly chemical in character, though specially classified just because of great importance. Most of them are far more important than carbon dyes or drugs. The per capita development of the U. S. in any of these branches is by no means backward. Unless one judges by mere number of paper patents it is hard to see how even the complete and absolute absence of two items like carbon dyes and compounds (81 million dollars) could make us "extremely one sided" with 1400 million dollars of chemical products.

When it comes to reasons for this supposed one-sidedness, we find, "And this is not for want of raw materials or other primary elements essential for the existence of such manufactures, but more so because both tariff and patent legislation have created a situation forcing enterprise in one direction and preventing it becoming engaged in the other." I wonder what this means. We have the same patent and the same tariff for dyes and fine chemicals as for hundreds of other products that aren't "backward." It is impossible to regard those laws as the sole or even the chief cause of the backwardness. Perhaps the figures themselves offer a true and ample reason in the mere number of patents that has caused so much worry. A business that required 300 patents and the unlimited research they imply when the gross business involved in each one promises to be only \$70,000 a year, does not appeal to the U. S. manufacturer. It breaks the Yankee heart of the average American manufacturer to spend money on research, but he will get over that some day. At present some very large corporations have the breadth of view to see the advantages. The ordinary company frequently fails in the first attempts and the small fellow generally becomes discouraged. The putting detail of such a business is apt to be scorned by large American companies. Admitting the aggregate value and the profit, still they simply do not care to go into it. Besides, our workmen are ill adapted to small manufacturers of fine chemicals. The few firms that are doing such work in the U. S. rely chiefly on foreign labor, particularly

German, Hungarian and Polish, and these men in spite of every effort on the employer's part to preserve their native conditions, rapidly change their habits and method of work. Versicherungs Gesellschaften und Turn Verein, 10 o'clock Frühstück, beer throughout the plant, etc., fail to preserve the faithfulness to detail, simplicity of life and economy of expenditure that prevail in the Vaterland and that are necessary to make such puttery work profitable. Thus we see that the number of patents in stead of showing the importance of the industry is only one of the evidences of the fussy character that unfits it for our special industrial condition—the fussy character and not the maligned patent system making us backward in this little field. As a matter of fact I am reliably informed that many of these German specialties are made with little or no profit even in Germany.

In its effort to hold the patent system responsible, the statistical paper contains a most remarkable implication: "*Unlike the heavy chemical industry, the manufacturer of fine chemicals derives its profitableness exclusively from patents.*" We are thus tempted to forget or ignore that in the sulfuric acid industry, patents cover all practical mechanical furnaces, the three really efficient dust collectors, the four most modern types of chambers, three of the four systems of concentration, and all available contact systems; that in nitric acid the Uebel, Valentiner, Guttman, and Jahn systems and all efficient direct synthetic methods are patented; that in muriatic acid every mechanical furnace has been and the two most improved still are patented; that the ammonia soda process and all the electrochemical methods were or are patented; that the patents of Hyatt Bros. founded the pyroxyline plastic industry and every new explosive is patented; that phosphate fertilizers originated in patents and nitrolime and cyanamide are now patented; that the archaic ammonia process is plastered over with petty improvement patents and that Haber, Frank and Caro and Serpek hold patents on the synthetic methods and products. There are a few other simple little facts inconvenient for the theories advanced in the paper—things that we are invited to overlook in plans for operating on our patent system. We shall try to see whether his oversight is accidental or is inspired by "corporations who have large interests in patented property" like the interest recently shown by a Mr. Berger who tried to have a bill proposed that no patent be granted for anything not already actually in operation (nice for a man of limited means with a dozen alternative processes or machines under one general invention). The paper tells us that "*The industrial and scientific progress of chemistry is to-day carried out in huge establishments by an army of workers, each contributing his share toward the whole.*" This may be true of the progress the author is most interested in and represents, but we have profound reason to be grateful that it is *not* true of the country as a whole. We still have men like Frisch, C. M. Hall, Acheson, Baekeland, W. H. Hall, Wedge, Townsend, Andrews, Ellis, Perkins, Wood, Toch and others far more numerous than the salaried inventors of the "Monopolies or Trusts"—men who have ideas on which new industries can be founded and have the character, the trained ability and the confidence of capital to found and foster these industries to independent success. These are the men who make the night-mare of a one-sided chemical industry very unreal to-day and are proving it false for the near future at least. Much as the paper under discussion seems to be antagonistic to monopolies abroad, everything it urges to do to our patent system means playing straight into the hands of the money powers at home and its recommendations if carried out would go far toward substituting the control by money, either foreign or domestic, for the control by brains fairly and squarely applied to alien and citizen alike. There are about a dozen large corporations in this country that would for a time profit immensely by the emasculating of the patent system and that openly decry and ridicule the rights

granted to inventors. The chief patent counsellors of these companies personally stand squarely for conservative and honest strengthening of the patent system and I would unhesitatingly trust the interests of both inventor and public to the decision of a majority of these men. Their personal consciences dictate their support. But their open and frank support may be quite as useful to the corporations, perhaps more useful than their opposition, for the ignorant public and the legislator shun the very wisdom that these men unselfishly offer. Meanwhile it behooves us, the public, to inquire how far these same corporations are trying to hoodwink the legislator ignorant of actual patent practice, how far they are actually leading him to propose the very destructive measures that are apparently intended to injure the large corporate interests and that would actually serve their best advantage. The majority of the Oldfield patent committee would perhaps be surprised to be considered tools of certain great corporations, but many a tool is quite unconscious of its function or motive power and every one familiar with existing conditions recognizes the reform measures proposed by these men as being framed perhaps unconsciously in the best interests of the monopolies. "By their fruit shall ye know them." Even the Lenroot "anti-trust" revision of the Oldfield bill (written in by the patent committee after the Judiciary Committee had thrown it out), much as it appears to be a blow at the "trusts," is actually a trust measure tending to abolish the only protection the small competitor has in his livelihood. Any and every form of transgression of any anti-trust law of Congress or of any state "however fantastic" is made the ground for invalidating any patent owned, used or licensed by the offenders. Inventors cannot even combine for mutual protection of their ideas. Small manufacturers or moderate sized companies cannot buy up additional patents for completion of their patent fences or possibly even employ inventors for that purpose. All that would be needed to invalidate the patent utterly is for the trust to get a license for one machine in one of its plants, or through one of its agents, and then commit or cause to be committed some petty infraction of some petty State law. While red tape and yellow legislation have already made invention a losing game, these bills would put a penalty on pioneering. The only gainers would be the "Trusts." They need no patent protection. Goliath needs no sword or armour, all he desires is to "get his hands on" David. And our legislators are trying to take away the little fellow's sling and smooth stone—his innovation in the art of war.

We should understand clearly a few things about the so-called "Patent Monopoly," "Product Patents" and this "Compulsory Working" and might as well include "Compulsory License" and "Absence of Price Fixing" also "considered" by our "economists."

You work, and have a right to the fruit of your labor. If you work with another man's materials and tools he has a right to a certain share, but if you work with knowledge and materials common to any one who cares to learn and to use them, if you apply your brains, get a new idea and use materials that you worked for and purchased with which to test the idea or make a model of it, then that new idea (process, apparatus, or product) created for the first time by you is YOURS. You can destroy by forgetting it, give it away, sell it for a thousand million dollars if any one can be induced without deception to pay that price, or you can cherish it as your own secret in your business and no living human being can justly object or legally compel you against your will to give it up to him. No government can grant it to you, because it was originally yours—you created it, or really grant you an exclusive right to it, for if you are truly the first inventor you have that right already, and can keep it unless by chance some one else works the idea out independently for himself (or steals it). Equitably speaking your title to it is infinitely better than your title to real estate given you, inherited,

purchased or even built by you, for you have created a new thing, not even copying some other man's method or idea. The right to intellectual property is the most just and fundamental right in this world. The United States first recognized it and on it is based our whole patent system. England granted Royal Patents to support the king on the one hand and on the other to induce the importation of foreign trades the starting of lines of manufacture not already operated in the Kingdom. The element of invention was unnecessary and incidental.

But even the United States does not actually give intellectual property one-tenth the dignity or security granted to Harrison's hog or an old overcoat. All civilized nations recognize the value of stimulating progress by publication of advances as made, of preserving an exact record of progress against accidental loss or destruction, and above all of encouraging progress to practical fruition by giving some one a special inducement to undertake the toil, expense and financial risk of commercializing progressive ideas and educating the people to make use of them. Unless used, an idea is worthless. Experience in Holland without a Patent system and in our own country with inventions dedicated to the public, has shown that the surest way to kill a new idea is to throw it open to everybody. It will not then be worth any one's while to work out the new thing and educate people to use it, for any one can come along and profit by the first man's planting and cultivating without any such effort or investment of his own.

So the Government—the people as a whole—say to the inventor: "Tell us all about this new thing promptly and fully and we will reward you and aid you and your associates in developing it practically by recognizing your right to it. Some one else might discover it sooner or later and might even develop it, so we can't make your right indefinite, but we will recognize it as yours long enough to make the development of it worth your while and give you a fair reward." The Government doesn't give the inventor a right to his invention—he had that by divine right. The Government (the people) only offers to permit a record of his title and thus save him for a time from the risk of others making the invention also, and give him a public grant so he may have the chance and the inducement to develop the invention, make it commercial and teach the people, provided, however, he tells all about it promptly and agrees to give up all claim to it in 17 years. In other words, the Government practically buys the invention for the public after 17 years and pays recognition and the right of excluding others for a time in order to induce and enable the inventor and his associates to develop the invention to a thing of public value.

Now, mark you, this service which we are seeking to buy from both the inventor and the investor is like every other service we buy in this world. If we are stingy the service will be niggardly. If we are tricky in our methods and cater to the legal chicanery that is always at the disposal of money power, we discourage and disgust the inventor and the investor, who will simply stop wasting time and money for nothing and either conceal the invention or not even perfect, much less patent it. If we offer good pay, well secured, we shall get good work. And we can't lose in the end. If the invention is good and well protected it will find money to develop it and the product will be sold at the price that will sell it most profitably, *i. e.*, quantity times margin of profit, in 17 years. If the invention is no good we do not lose anything but if the patent we grant is worthless, no one will touch it, and we have robbed ourselves. Perhaps a monopoly in some related field may take it up, protected by the power of mere size or wealth, but no small manufacturer will be protected in the fruits of his effort. Whatever security we may give the inventor, the invention reverts to us, the public, in 17 years. The only question for us is, shall we inherit a good useful industry or a property that no one has dared to improve because

of imperfect title or sterile soil? Such is the "awful monopoly" granted by the Government."

This "product patent" question is, after all, mainly a question of whether we desire to encourage all inventors, rich and poor alike, or only encourage the big corporations and trusts. Only the big fellow who finds a new compound can afford to put 20 men to work at once on all possible ways of making it and pay big attorneys' fees for carefully drawing a dozen patents if need be. The product patent is the poor man's best protection in the U. S.—almost his only good protection with the complicated legal procedure we have here. We have a frequently repeated fallacy that there is no product patent in Germany and that her chemical development is one consequence. Let us see how it works. The German Law Amendment, 1891, Art. 1, Sec. 2, speaking of patentable subjects says "exceptions are substances manufactured by a chemical process in so far as the inventions do not relate to a distinct process for manufacturing such articles" and Sec. 4, "If the patent is granted on a process the operation of the same is extended to the direct products of the process." So, if you can afford to employ clever experts and clever lawyers who will study with care the essential steps in the various ways of making the new product and draw a single claim broad enough to cover them all, the *product* of this "distinct process," however broadly expressed, is patentable even in Germany. I know this to be not merely possible but actual practice, for I have done it for clients. It is expensive. In one case (a single patent) the attorneys' fees were about \$2,000 and mine was not smaller. That German patent cost about \$10,000 and the first claim of 10 lines took five of us over a week to express exactly right. In this case one broad patent was calculated to be cheaper and better than the 15 or 20 narrow ones that might have been used to cover the same ground. I think you see how it works to the detriment of the inventor who is poor. Figures absolutely confirm this statement. Quoting directly from the paper in question, "*Of all patents issued to Germans living in Germany 75.5 per cent were assigned before issue. The highest ratio of these assignments is reached in carbon dyes, about 98 per cent.*" Further the paper states "*Of 1754 (total) patents issued for German inventions, 1247 or a little over 71 per cent related to carbon dyes and compounds and bleaching and dyeing processes, only 5 subdivisions out of 40 considered in the table. The number of those assigned out of 1247 was 1111 or practically 90 per cent, and of these 844 or 68 per cent were assigned to only 4 companies, who in connection with one other company work on a 'Community of interest' plan, by an interchange of stock and division of profits under an agreement to last 50 years from 1904,—one big trust.*" It looks as though the German trusts "got 'em," whatever they are worth, and as though in Germany practically the only inventing worth mentioning (in these lines particularly) was done by employees of the big corporations. What better proof could be desired that the much lauded German system of no product patent is a sweet sop to the big corporation? On second thought you will hardly prefer the German method.

"Compulsory working" has become a farce in every country that tried it except England where it hasn't been going long enough to become systematized. Elsewhere it is generally a matter of a little money to formally comply with the statute by advertising and laboratory work without really establishing the industry in any true sense, the approximate cost per year in Germany, France, Belgium, Sweden, Italy or Russia being a couple of hundred dollars. England has recently started it. Let us see how, according to statistics, this newest and most drastic compulsory working law has operated during 3½ years. What has it produced? About 50 foreign firms have complied with the law, about 4 million have been thus invested and the yearly pay roll of Great Britain has been increased about 2 million. These figures may appear large but are only 0.1 per

cent of the invested capital and 1 per cent of the annual pay roll—an increase of 0.03 per cent and $\frac{1}{4}$ per cent, respectively, per year. Why, the suffragettes alone cost England much more than this four million dollars last year, in a single year. Some foreign firms would have put up plants anyway and the whole result is practically negligible. But the report goes on to say: "This did not include the large number of licenses granted by the patentees to English manufacturers under the best conditions obtainable choosing the alternative rather than suffer the repeal of the patent," *i. e.*, patents given away because the fool statute had made them practically worthless. Nor does it include the larger number of patents allowed to forfeit and become public property—hence worthless to anyone. Holland had the benefit of the patents of all nations for years but never developed a real industry herself until she passed patent laws to foster it. England is unquestionably doing her industries more harm than good (which as we have seen isn't saying much). Her people will unquestionably be charged the additional price to reimburse those foreigners who started this \$4,000,000 worth of factories and she will lose more than an equivalent number of other industries by her confiscating policy. Germany tried the abolishment of compulsory working for U. S. inventors and recently made up her mind to abolish it quite generally, as more harmful than helpful. It will probably take England two hundred years to find this out. Why should we imitate her? Also it is said of France, "Many firms engaged in chemical industry in that country are controlled by foreigners largely due to the compulsory working feature" as though it were a desirable condition of things to have our business and manufacturing enterprises controlled abroad and sending their profits out of the country. Most of us think not. Probably some protection should be devised against a certain form of abuse—the German patents a product here, supplies our market exclusively by importation, not manufacturing here at all, and charges us an exorbitant advance on the regular price in Germany. A provision modelled somewhat on the Canadian law might help matters, *e. g.*, all patents of foreign invention shall be subject to the compulsory grant of license to United States manufacturers at royalties to be established by the Federal courts whenever it can be shown that the product is chiefly manufactured abroad and is sold in the United States at prices more than 10 per cent in advance of corresponding prices in the country of manufacture plus reasonable cost of transportation. This would seem to meet the condition most complained of by the drug and fine chemical trades without unjust confiscation of the inventor's rights. The present situation is, in some cases at least, chiefly our own fault for not contesting strongly enough a grant which really trespasses on the public domain.

Compulsory license would give others the right to sue the inventor or manufacturer for a license whenever the demand was not fully supplied. The large corporation could create a false demand, storing the goods for a few months. The patentee and manufacturer must increase their plant to meet it or give a license to a powerful competitor. And about the time the added plant is completed, this stored product can be pushed on to the market and both new and old plant held idle for months. Or else, if the license is granted by the court when the new invention is just developing its market and just getting down to a tolerable manufacturing cost, what chance is there of getting a fair royalty? And if the patentee and his capitalist win their suit they would be subject to innumerable suits for granting of license by any one to whom the large corporation cared to lend its legal staff for the purpose. A law against unfair competition has helped to protect pioneers in other countries, but we have no such law. In the U. S. there would be no use in inventing at all or trying to exploit inventions except for employees of the large corporations. In Germany "compulsory license" is to prevent the sup-

pression of vital military, naval or medical inventions by foreigners and there has not been one compulsory license granted in 11 years.

Finally, it only requires the removal of the right to sue as infringement the cutting of fixed retail prices upon patented articles to give the inventor and his manufacturer absolutely no protection against ruin by unscrupulous interests. A few thousand dollars worth of his goods purchased by the big corporation (or by some jobber at its instigation) and scattered in small lots to the cut rate advertising department stores can utterly demoralize the carefully built up trade and cause the goods to be thrown out by every retailer in the country. And the inventor or manufacturer would have no recourse except to mortgage his factory and spend the proceeds in multicolored litigation under the kaleidoscopic statutes of 48 different states. As it is to-day, all sorts of standard articles of established repute and price (therefore particularly patented articles) are selected as the bait for cut price sales in all parts of the country—sales at which the standard articles (with very few in stock) are largely advertised at 30 to 50 per cent below cost to induce people to come into the store and after which they are persuaded to buy something "just as good of our own make because we have sold all that particular brand" and pay for this substitute twice what it is worth. No surer or quicker way of ruining a business can be devised than starting the price cutting of its standard product. The consumer always suffers first because price cutting is advertised as a lure to actually sell some relatively worthless substitute; second, it disgusts the retailer of the standard goods who declines to handle them; third, it ruins the business of making good qualities, leaving only the worthless article to cheat the public. The merchants associations themselves favor price fixing (Cong. Hearing, 4/24/12, 5/2/13 and 5/16/12). Recently the Supreme Court (Bauer v. O'Donnell) decided that the present law gives the inventor no right to sue such pirates as infringers, in other words, no adequate protection. Who is most hurt by this, the "Trusts?" No. The Eastman Kodak Co. is reported to have advised retailers that they must become exclusively Kodak agents or lose the entire line. And they "become," without expense or inconvenience to the Kodak Co. This leaves the small independent more helpless than before, without any similar protection, and we, the public, may go without independent goods. If this is the law, we may well change it.

In considering these four proposals with regard to our patent system, or any others, for that matter, one great fundamental principle should, however, never be forgotten, *i. e.*, the principle of preserving the right and title of the inventive creator to his intellectual property, at least as perfect as the title to chattels for the limited period which is agreed upon as a just and expedient reward for his contribution to human progress. Our prevalent ideas with regard to intellectual property rights are almost aboriginal in their crudeness. With the development of a clearer title to intellectual property, industrial life may look forward to as great a stimulus as social and business life has received by the securing of real and personal property right. In the stone age when individual might made right there was little incentive to save or traffic or invest. The world has but recently (about a century) conceived the right to intellectual property in a vague way. Look at the relative industrial advance that has resulted and conceive if you can of the progress when brain property is as secure as real or personal.

Consider: We, the Public, go to the inventor and capitalist to induce the former to reveal his secret knowledge and abandon it to the public in 17 years and induce the latter to put his money into the testing, development, manufacture, marketing, and education of consumers to use a new and untried invention. We can't reasonably expect this service unless we really give:

1st. A patent obtainable at reasonable cost with the least

possible delay and expense of needless technical stickling or the possibility that catch-penny attorneys will abort a patent application to get their money easily. We should further eliminate the enormous delay and expense of interference proceedings, by considering only the first applicant (except in case of fraud).

2nd. A patent that is what it claims to be, a certificate of absolute right in novel property, an agreement between the public and the inventor, his heirs or assigns, "to keep off the grass" entirely for a limited period because he grew the grass; a patent that has been so carefully searched that its presumption of novelty amounts almost to a certainty, and then exposed to public contestation so we all have a chance to object to possible preemption of public property and practically consent in the grant.

3rd. A patent that, as a certificate of private property is really enforceable, like any other property right by the public that has consented in it after liberal advertising of the proposed grant. If some fellow grabs your pocket book, or automobile, or horse, all you have to do is to make complaint and the People take up the case. All that you have to prove is that he took it. To avoid fine or imprisonment or both he must do all the proving of any right he may have had to take it. There is no reason why properly certified intellectual property should not have equal rights with any other personal property.

All this patent revision work should be in the hands of a Special Commission of diversified character to be selected by the President.

Though larger in number, the patents for mechanical devices that can be imitated are much smaller in value to us, the public, than the processes and products which can be operated secretly or disguised to a very large extent and in the use of which (unless patented) the large corporation can always beat the small manufacturer or the inventor. Public welfare demands that we learn about them all. Without patent protection no small concern or individual will find it worth developing unless it can be kept secret. Public welfare demands the development of industries. We want improvement and progress actually carried out in industries and commerce and not mere paper inventions. Remember that every cutting down and restriction of the inventor's right for his short exclusive period cuts down the right he is able to give the investor, and that we need the investor's interest in the invention just as much to make real progress. We may trick and bamboozle the inventor, not the capitalist. And remember above all that national interest, integrity and self-respect demand a clear development of the same right to intellectual property as to material chattels. The great IDEA is quite as valuable and dignified as the great American Hog.

No truer word was ever spoken of our industrial progress than the oft-quoted statement of Kasier Wilhelm to the late Henry W. Draper, "There are three causes for your (American) wonderful industrial progress: your native ingenuity, your great natural resources and your admirable patent system. But the greatest of all is your patent system." Lately, however, our patent practice has become wound up in legal red tape until it has almost lost stimulative effectiveness, our resources have, until recently, been thoughtlessly squandered, and our native ingenuity is better evidenced by variety and multiplicity of proposed laws and cunning methods of avoiding them than by simplicity and obedience. And now there has arisen a new madness from within and a new menace from without. Within, our restless ingenuity for legislative blunders in turning its attention to the patent matters refuses to see the need of a Commission of legal, technical and business experts and ardently pursues any phantom reform that threatens to emasculate the whole system. Abroad, the recently adopted patent law of Holland is already bearing fruit in industrial development where the greatest merchandizing nation of history is prepared to bring

the products to our shores. Germany with eminent advice from all classes interested is remodelling her already excellent and simple patent laws to surpass our own. Japan with 50 million population and very cheap labor now has a well studied, carefully executed patent law in some respects better than our own, and is developing wonderfully her industries, and China will before long turn her 400 million thrifty people and very great natural resources including enormous coal fields into competitive industry.

Manufacturers of the United States, unless you look around you and look ahead, no tariff will protect you long with certainty. The people at large insist on having the world's products at a fair price and if you neglect your birthright it will be Another's to make these goods. The people may vacillate in their opinion, but that is industrially worse than continuous free trade. Without the stimulus to your own country's brains which security of intellectual property rights alone can give, you will as surely run down to stagnation as the unwound clock. The inventor and the investor in new inventions, alone, can keep our industries in the van of progress. We may fool the inventor with insecure patents but not the investor and we need the investor just as much as the inventor and must make secure the rights of both. If you sit idly by and suffer chromatic legislation to emasculate the patent system the ingenious legislators will write the death warrant of your industries and your business. And, mark you, it avails you little to make steel, or clothes, or some other thing "not based on patents." The success and prosperity of the country at large are the real foundations on which your prosperity rests and the failure of the man who needs your steel or the man who weaves your cloth or buys your clothes will carry you down with him. If "it only hurts the other fellow's business, not ours," you cannot avoid your part of the penalty brought by destruction or degeneration in other lines of industry.

One of my former clients shrouded and laid away his business some years ago because German invention had outtripped him in more than half his products. The president of another client told me recently that Japanese products were beginning to be offered his customers at little more than half what it cost him to make them. Why not, with ample supply of cheap raw material in China and Japanese labor at 15 cents a day? He "had never thought much of patents" but confessed "I wish we could protect our products to-day." You manufacturers may not see what good a simple, easily enforced patent system would do you directly to-day; most of you do not realize that almost any material advance you make in an art, is protectable if properly presented by really good patent attorneys (none of whom by the way is any cheaper than the really successful lawyers in another line). To-morrow may bring that special improvement in method or quality of product that would help to assure the safety of your business for 17 years, if your right to intellectual property were secure. Next year is as likely as not to establish beside you a new industry that for 15 years will supply a new and cheaper material for your plant or else take the greater part of your output for its special use. And the special use of the new material or adaptation of your product is almost sure to be wholly or in part protectable by patent. Will you take title to the intellectual property that is really yours or merely be a squatter till foreign competition (if not domestic), till cheaper labor or better stimulated brains can drive you out?

Your only permanent safety in the future lies in the preservation and perfection of the U. S. Patent System for the only sure stimulus to effort is security in the fruits of effort.

No temporary "influence on legislators" will stem the tide. It worked for a few years with the tariff but, within ten years after direct popular education on tariff matters gave place to political jobbing, the mass of people ceased to understand. Where is there any assurance of protection to-day? Whatever

new idea you conceive that improves your process or the article you manufacture, should be as much yours as an overcoat you buy. Your title should be as clear and simple and well recognized for a reasonable time and your right to protection by public prosecution at least as good as if some one stole your overcoat. A few of us are trying to educate 60 million people to understand that the future of this nation and their own individual prosperity depend directly on the security of intellectual property. You would do well to start the regular education of your workmen, for it is the uneducated vote that puts in the destructive legislator. Your Board of Directors had best appoint their brightest man a "Patent Committee with power" to lend a hand. Get an intelligent Commission, have its findings published broadcast for discussion so the average voter may understand the issue and the Congress dare not ignore anything the Commission recommends.

50 EAST 41ST ST., NEW YORK

"WHAT'S THE MATTER WITH THE AMERICAN CHEMIST?"

By DANIEL M. GROSS

Received May 16, 1913

A recent news item in the daily journals should furnish food for some very serious reflection. In brief, it stated that the American textile manufacturers have for years been under the domination of the foreign dye trust and are at last beginning to revolt. Why this industry is so dominated, why they have not revolted heretofore, and what their revolution will bring forth are well understood by any person who has studied the subject and is familiar with the status of commercial chemistry in America.

The industry mentioned is forced to use large quantities of imported dyes because they are superior to most of the domestic dyes and are also forced to pay \$1.00 per pound for a product for which they formerly paid 25 cents.

What's the matter with the American chemists that they cannot supply their own market? Is it possible that they cannot, with all their vaunted genius and mechanical ingenuity, and with the protective barrier of a high tariff, exclude these as well as other articles of foreign manufacture?

To acknowledge we cannot make as good products as foreign chemists is not only humiliating but true, not only in the chemical industry but in others also and the reason for it is that the foreign producer has worked on the basis of making the best goods at the lowest cost and makes them under the intelligent supervision of modern science.

American chemists individually are just as brilliant, well educated, energetic and ambitious; hence the cause is elsewhere. Our educational institutions are surely competent and possess the necessary facilities, so where does the difficulty lie? Simply in the fact that science has been relegated to the rear and that the American chemists do not get the encouragement and co-operation needed to develop their activities sufficiently to meet commercial requirements.

Our manufacturers have been concerned primarily in producing goods to make money and have always had every advantage in their favor. A large demand due to an increasing population, plentiful and cheap raw material and fuel, efficient machinery and mechanical appliances, shrewd financial management and business combinations and again the highly protective and benevolent tariff. We have never felt the heavy hand of competition as have English and European producers and yet with every advantage we cannot produce first-class goods.

Germany's encouragement of the chemist, both financial and educational, and the application of scientific methods to industrial needs in general and chemical productions in particular, their eagerness to utilize any new knowledge in their factory operations, and most of all a willingness to spend money in experimenting and developing ideas and processes, are the reasons why that nation to-day is gradually absorbing the

commerce and business of other nations. France long ago realized her danger and is rapidly applying science to industrial ends and even Italy, a nation of supposed lethargic temperament, is keeping in the front rank.

England has already felt with much concern the iron hand of the Teuton reaching out over the seas and gathering in the business of the world and our turn will be next. No less authority than Prof. Perkin recently stated that these are indeed parlous times, and England's commercial future depends upon scientific industrial chemistry and to that alone the nation must turn.

It is no exaggeration to say that the situation in America at the present time is chaotic. The complaint of the textile industry is characteristic and confirms this assertion in their single charge that they cannot get domestic dyes of quality and are being plucked for what they are forced to import.

The American producer is laboring under the impression that when he attains mechanical perfection in his factory he has all that is to be had. Mechanical contrivances are well and good, but they are only a small part of modern industrial operation. Nearly all operations are dependent upon raw material; raw material is substance and that in its turn is chemistry, and every industry or process involved is to that extent chemical; wherever we turn this fact stands out most prominent.

From the very nature of things, education to-day is largely a matter of books, and while much valuable information and training are obtained from this source, there is one vital element to success, not only in chemistry but in other professions, which is often neglected. This element is called common sense but experience shows that it is indeed far from being common.

In solving the industrial problems of to-day its intelligent application is equally as important as professional knowledge. It is no more possible to solve a chemical operation of magnitude by abstract principles than it is to diagnose a disease, repair a mangled machine or conduct a legal case.

In no other country but Germany does there exist such co-ordination and co-operation between the industries, institutions of learning and finance. A typical instance may be given in the discovery, by a German teacher, of a new process. His first effort was to present it to the expert of a great factory concerned in its production, then to the great financial institution of Germany, the Deutsche Bank. As a result, the factory with its producing facilities, the bank with its backing and financial aid, and the discoverer with his process form a company of three.

Imagine the reception a chemist approaching a bank in this country would get! Nothing is harder to get in this country than financial assistance to develop a chemical process. Many individuals have the idea that chemistry is merely a routine operation, and it is no secret that a chemist in developing an industrial process has his own troubles. Numerous instances can be given where the establishment of a factory laboratory would save thousands of dollars to the producer, but he apparently prefers joggling along in the "save at the spigot, lose at the bung" gait of his forefathers.

Any process to be of industrial value must be perfected on industrial lines and while a laboratory reaction will give all that may be desired, the same reaction with tons of material to work with instead of grams, means something different, as many have discovered to their confusion and sorrow. Many operations successful in the laboratory have been a failure when conducted on a large scale and the chemist condemned along with his process when the fault could have been avoided by an intelligent application on a different basis.

Chardonnet made a dead failure of his artificial silk process when he tried it out commercially, not once but four times, but financial assistance was given him, instead of condemning him as a fraud or fakir, and the process as a swindle. German chemical firms spent millions before a dollar's worth of goods

was marketed. The chances are that an industrial chemist in this country who could not revolutionize conditions or produce ideal results in a few months time, would be fired for not knowing his business.

So much stress has been placed upon the value of chemistry in the industries of to-day that the majority of people have the most vivid ideas concerning it. They do not know that each application of its benefits meant perhaps years of persistent and unpaid toil. An individual once came to the writer to perfect a certain process which would ultimately devolve into a business of enormous proportions. When informed that a sum of money would be required for a special laboratory, trained workers, equipment and material, it almost produced apoplexy. He was ready to benefit but would not pay research expenses, had no idea chemistry involved such work, required such time, etc.

Certain conditions exist in the commercial world of industrial chemistry that are inexplicable and almost ludicrous. Why do we import essential oils to the value of millions each year when we have all conditions, climatic and otherwise, for their domestic production? Why is impure bauxite imported by shiploads when we have aluminous ores, rich in alumina, free from iron and calcium by the millions of tons in our own land? Why do we use the chemical process for producing the enormous quantity of alum consumed, when from the same source pure sulfate alumina can be loaded on cars like sand from a sand-bank?

No wonder foreigners say we are insensible to and unappreciative of the good things nature has provided. No fault can be found with the American chemist individually, but the system or promoting and developing the chemical industries and applying science to commercial requirements, needs a severe and an awakening jolt unless we want to be brought to our commercial knees.

5927 WALTON AVE.
PHILADELPHIA, PA.

GENERAL EFFICIENCY IN DYEHOUSES AND BLEACH WORKS¹

By LOUIS JOSEPH MATOS

It has well been stated that the enemy of waste is efficiency, whether of labor or machinery. If the kind and character of labor engaged in any work is of the highest order commensurate with the character of output, just so high will be its value, and likewise, if the tools and appliances made use of in forwarding the raw material from one process to another are of the highest possible type suited to the purpose, so again will the condition and quality of the output be high in proportion.

Perhaps in no industry is the force of the above statements more apparent than in the conversion of raw textiles into finished fabrics, whether they be cotton, wool or silk, and in no subdivision of these industries more so than in the dyehouses and bleaching plants. Other departments of textile mills contribute their share of skill to the value of the ultimate fabric, notably the finishing department, which has more to do in the physical handling of the goods than other departments, and consequently its treatment may be safely omitted at this time.

The dyehouse of a modern textile mill is in reality a huge laboratory where the raw stock, yarn or piece goods of whatever fiber made is colored to meet certain commercial demands. It is in this laboratory that the material to be dyed is generally prepared for the actual dyeing operation by such treatments as will better enable it to take the mordants or dyes as the case may be. This preparatory treatment consists in the majority of instances in cleaning or scouring the goods free from all extraneous oils, grease, dirt, etc., that become attached to it unavoidably in

its passage through the mill, or which may have been added to it intentionally, such as oils in the case of wool. Consequently it stands to reason that if the dyer is expected to turn out good work it means that the goods delivered to him should be clean; that is, thoroughly scoured out, or boiled out, with either soap or soda according to the stock, and then finally rinsed. Here the lack of efficiency in many woolen mills is painfully apparent; through misdirection or otherwise, scouring in alkaline soap liquors is pushed to the limit under the mistaken idea that hard punishment of the pieces is the best means of removing oils and dirt; this is followed by failure to give the best part of the scouring—the final ample washing in water, so ample as to remove all traces of the emulsified oils and the emulsifying soap liquors. Absolutely false economy is experienced by such treatment of woolen or worsted goods, for the reason that traces of soapy liquors remaining are the unmistakable causes of so-called cloudy or streaky goods; defects that cannot be removed and can only be hidden by over-dyeing with other and heavier shades or by stripping and re-dyeing. Two definite results are then obtained: (1) The goods are not of a level shade, and consequently, if otherwise acceptable, must be sold at a lower price than they would normally command; (2) If they are stripped and re-dyed, other conditions of feel, handle, texture and shade being equal, the time and the cost in re-handling and re-dyeing are absolutely lost, and cannot be recovered from the buyer.

Efficiency in the preparatory treatment of woolen fabrics therefore resolves itself into thorough scouring and perfect rinsing, without which no piece of goods is ready to be dyed. Perfect scouring, again, brings pointedly before us the necessity of having good water to scour with. Some mills are so favorably situated that their water supply is of very low hardness and generally free from suspended matter, but, on the other hand, there are many mills that have only a moderately soft water and some where it is liable to be contaminated with much silt. Where the water is clear and soft, or moderately so, no bad effects are to be found in the goods due to the water, but under the mistaken idea that cheapness is an element of economy, some mills having an unlimited supply of good water use mill soaps of the lowest grade, rosin filled, with the result that the characteristic odor of rosin persistently remains with the goods, whereas if even a fair quantity of tallow soap had been used, the goods would at least be free from odor if well rinsed.

The importance of water softening in connection with dye and bleach works has not reached the position it deserves, but as competition increases among textile mills, and the demands for relatively better fabrics from a constantly discriminating public increase, the mill that aims to meet these particular demands will be the mill to avail itself of every scientific help. It is a fact that there are to-day otherwise practical mill men who conscientiously believe that the tenaciously adhering lime soaps, the result of hard water, are effectively removed in a competitor's mill and regard with sincere distrust the statements of chemists that such deposits when formed on wool are irremovable, when such deposits are found on woolen goods in their own mill. Irrespective of the saving in the cost of soap, which could be credited to increased scouring efficiency, the amount so saved would in many mills be the interest on the money invested in an effective water softening plant.

Modern ideas in textile machinery have in general kept pace with other improvements, but there are many large mills that, years ago, turned out goods that held a prominent place in the market, but now these do not meet with the same favor as goods from other mills. On examining the cause of this condition, we are confronted with the fact that the machines used are of types long since discredited and abandoned. This applies to scouring as well as to dyeing. The old type of woolen goods washers, found in many mills, depended upon their harsh and energetic

¹ Presented at the Boston meeting of the American Institute of Chemical Engineers, June 25-28, 1913.

treatment of the cloth itself, leaving the solvent and detergent action of the soap and alkalis used to take care of themselves, whereas the more advanced type of appliances is so constructed as to give the soapy liquors the very freest action, without in the least impairing the condition of the cloth. Scouring of woollen goods is essentially a chemical process and not a mechanical operation.

Economy in the dyehouse proper may be effected along various lines, but each should be so considered that it fits in perfect accord with all other lines, so that there may be a maximum output of clean dyed goods ready for the dry-room or finishing department.

Dyehouses in which the labor, that is, the so-called kettle hands are not identified with their work, can never work as smoothly as those where the workmen are made to feel that they are a part of their department. Perhaps in no other department of a mill is the personal equation so much in evidence as in the dyehouse, and it should be the one where there is the least discord.

It was formerly the case that the master or "boss dyer" struggled under great difficulty to acquire his fund of information and this he, perhaps with good foresight and intention, preserved with great care to himself. He was on close personal terms of intimacy with his several helpers, the most ambitious of whom, ultimately and in turn became a "second hand" and was taught the principles of the trade, which in reality were the names of the "drugs," from whence obtained and how prepared for dyeing. This condition of affairs held up to the discovery and introduction of mauve, Perkin's discovery, from which time to the early eighties the so-called secrets of the dyers have gradually vanished, due in a great measure to the immense amount of practical technical data that is freely disseminated to all inquiries by the large color manufacturers. Consequently, the dyer of to-day is a much better technically informed individual than his earlier prototype, of which latter, however, there are a few still holding over; while realizing that important discoveries have been made, they still endeavor to convince themselves that the older methods were the most ideal.

Dyeing efficiency means getting the most out of a dye or given group of dyes. This means that the dyer should be sufficiently well informed by study and experience gained in a laboratory, to be able to recognize when a dye is yielding its best, and not stop at being merely a shade matcher. It is just here that the management of mills fails to secure proper efficiency in their dyehouses, believing that output is the only factor by which efficiency can be safely judged.

The purchasing department of a mill, notwithstanding the great amount of really valuable and authentic literature that is freely placed at the disposal of the color makers, cannot be expected to be fully informed as to the properties and characteristics of dyestuffs, as it requires special knowledge and training. To be intelligently informed regarding identity, tinctorial value and other properties requires laboratory aid of various kinds and a true index of mill efficiency is the use made of a well ordered laboratory.

One very large mill is gradually solving the problem of dye-house efficiency in a manner that should serve as a model for all textile mills using aniline dyestuffs.

The equipment of this laboratory comprehends every phase of color testing, not only for the matching, of dyestuffs, but also for print tests. The system adopted is one which is perhaps the most practical that could be selected. Dyestuffs submitted to it are classified according to color and as nearly as possible according to shade. They are then dyed upon their standard woollen yarns, parallel shades of the same percentage strength. The object of this test is to determine whether or not a given dyestuff is stronger in tinctorial value than another. This test is supplemented by a further test showing the money value of

two or more dyestuffs, the object of this series of tests being to ascertain whether, color for color, one dyestuff is cheaper or more costly than another. After having determined the relative tinctorial values of the series of dyestuffs, dyeings are made to show approximately the same shade and depth of color; then the yarn suitable is wound on cards of a few inches in width with bands of the several dyed skeins and these exposed to the light for successive periods of seven days. The result of this series of tests then shows conclusively what dyes resist to the best advantage the action of direct light and those which succumb to this treatment. The entire system of testing dyes by this apparently complicated though very systematic method works out to the very best advantage of the mill; when the results are placed side by side, the chemist, the dyer and the designer have at hand all the available technical information necessary regarding the utility of any one particular dyestuff, and are consequently in a position to eliminate, according to the laboratory tests, dyestuffs which will not withstand the later and detailed processes upon the finished fabric. This particular phase of the laboratory's work serves as the most important lever to the dyehouse desiring to give the greatest efficiency to its mill.

A careful, systematic and thorough examination of any dyestuffs or groups of dyes of apparent value in a mill coloring textiles can be satisfactorily ascertained only by subjecting them to other kinds of tests that technical practice dictates. After having survived the intelligently conducted tests in the laboratory, the survivors may then be passed to the large laboratory, the dyehouse, or the print works with the fullest confidence on the part of the dyer or color mixer.

In the mill in question not only are the dyes so thoroughly tested, but the compound shades in which the fittingly surviving dyes are used are also made in the laboratory, the exact proportions being worked out and submitted to the designer. If the shades so produced pass the scrutiny of the designing room, all the information necessary is then passed on to the dyer who makes use of the foundation formula, worked out in the laboratory; this results not only in a great saving of time in the handling of goods but also in economy of dyestuffs. The surviving portion of the dyed skeins, print tests and exposure tests are systematically filed according to color, and are open to access to every one having business with the colors.

The buyer in this mill is consequently in a position to discuss intelligently, and in the best interest of his employers, the question of dyestuffs, and consequently is in a better position to judge on the merits of the various colors after having passed through such a systematically conducted and well ordered laboratory. Generally, the laboratory of a mill has been regarded as a needless expense, itself in the class of non-producing departments, but mills striving to maintain a position in the forefront of manufacturing excellence are beginning to regard a well directed and properly equipped laboratory as one of the most valuable additions to an intelligently directed purchasing department. The two must go hand in hand.

As a general rule, American mills have not been as prompt to look into the merits of the various types of dyeing and bleaching machines and other apparatus designed to facilitate these two important operations, as have European concerns.

Without specific reference to any type or system, there have been brought to successful operation various forms of dyeing machines that are a great advance over the usual kettles and other appliances used in dyeing; the installation of these tends materially towards advancing the efficiency of the dyehouse.

It is a matter of fact that any dyeing or bleaching machine that conserves the condition of the textile material under treatment, other things being equal, is the ideal machine to adopt. When the mechanical handling of textiles during the bleaching and dyeing operations was first given attention by engineers,

the one serious difficulty encountered was the very defective physical condition of the finally dyed or bleached material. These defects, however, were gradually overcome by means of various expedients so that at the present time there are a number of machines in use that imitate identically the best results that it is possible to secure by means of hand work.

This type of machine is included in rather a wide group of others embodying the broad principle of working the material to be treated in the dye or bleach liquor, and generally requires a larger volume of liquor than other forms of apparatus.

Another group of machines is those based on the broad principle of circulating the dye or bleach liquor through the material to be treated, either with or without pressure, the result of which is that the dyeing is accomplished without any disturbance whatever of the condition of the material. In the early days of this type of machine, many set-backs were encountered, due chiefly to lack of penetration of the material by the liquors; thus many such machines were generally condemned. As experience was gained, it was found that the defective results were due entirely to a total lack of knowing how the apparatus should be loaded and packed; loose and indifferent packing always caused uneven results, while hard and close packing—leaving but small chance for leads and channels—always gave a dyeing or bleaching that was as close to perfect as possible.

Still another class of machines found especially valuable for loose wool is somewhat intermediate between the two general types above referred to, and consists of holding an amount of raw stock without any attempt at packing, and circulating the dye or other solution through it. The result in this case is a thorough dyeing of the fibers without any felting—a most serious evil, especially when handling the middle and higher grades of wool.

Reference to these mechanical aids to the dyeing and bleaching operations is made only for the purpose of drawing attention to what does exist, and the fact that there must be a demand for them sufficient to induce inventive dyers to go beyond the usual antiquated apparatus. From the common open kettle for skein yarn, in which the yarn is turned by hand, and which is in use to-day in many mills, to the crudest type

of mechanically operated yarn kettles is a long stretch, but the later devices are gradually growing

For years, and even to-day, the usual custom of handling warps in the dyehouse is with open tubes and "boxes," through which the warps pass under and over submerged rollers, and it has only been of recent years that serious attention has been given to the dyeing and bleaching of warps "on the beam" that is, in spool form. The warps are wound tightly to the extent of many thousand yards on a special beam (spool) and by means of proper pumps the liquors are forced under pressure through the mass of wound threads. This principle of bleaching or dyeing is now only in its infancy, and I believe that in time it will be developed into the ideal manner of dyeing. While cotton cloth cannot be successfully dyed by this principle, it is quite possible to bleach by it, and it is not to be doubted that ultimately pieces may be dyed successfully in the same manner.

The textile industry is stimulated by constant competition, mill against mill, and while some mills appear to succeed with certain lines of fabrics, others making similar lines seem to be unable to forge ahead. In quite a number such instances, careful investigation had shown that the difficulty to be overcome is the stoppage of leaks and losses in the handling of the goods, in and from one stage of operations to another, and by changing from obsolete methods, both mechanical and chemical, to methods that are modern and more in harmony with the spirit of the times. Many dyehouse and bleach works are absolutely non-efficient when compared with other departments of the same mill, and this is due in the majority of instances to the non-progressiveness and parsimonious policy of the mill, and also to the lack of initiative of the department foreman, who lags behind by not applying the advanced advantages of his particular line of work; in consequence, this department also lags behind—a millstone or an anchor—holding back the general progress of the mill. This is the condition that to-day confronts many of our apparently advanced and progressive mills.

103 NORTH 19TH ST.
EAST ORANGE, N. J.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE CONSUMPTION OF OXYGEN

It is estimated in *Chemiker-Zeitung*, 37, No. 69, 703, that the consumption of oxygen this year in Germany for the autogenous welding of metals alone, has already exceeded 10.5 million cubic meters, and the opinion is expressed that this application will be considerably extended. A few years ago the utilization of the hydrogen resulting from the electrolytic decomposition of water was not extensive, although large amounts were consumed for various purposes, as in the incandescent lamp industry, in glass blowing, in dirigible balloons, etc.; still the demand was only such as had no noteworthy influence upon decreasing the price of oxygen. Since then, however, new industries have appeared which utilize large quantities of hydrogen, as, for example, the soap industry, where it is employed for hydrogenating oils. The Knowles Oxygen Company, of Wolverhampton, England, has closed a contract with the Sunlight Soap Factory, in Port Arthur, to erect an annex to the plant for the production of the hydrogen necessary for hardening palm oil; the oxygen is to be sold. Plants have also been erected by the Knowles Oxygen Company in Wolverhampton and Sheffield, England; in Osaka, Japan; in Sydney, Australia; and in Brussels, Belgium.

HARDENING STEEL WITH COMPRESSED AIR

A process whereby steel is hardened by means of compressed

air is now in use by a German firm in cases where only certain parts of the metal require hardening. The customary methods of hardening by chilling the steel in water, oil, or special baths is not satisfactory in such cases, owing to the tension created between the hardened and unhardened portions of the treated metal. In the new procedure the compressed air is sprayed over the metal through specially designed nozzles, by means of which, by varying the number and spacing of the openings, the degree of hardening may be accurately graded. The claim is made that a wide range of results can be obtained by adapting the shape of the nozzle to that of the work.

THE PRODUCTION OF VANADIUM STEEL

While in 1905 the approximate total output of vanadium steel amounted to 800 tons, last year 90,000 tons of vanadium steel blooms, billets, bars, forgings and castings were produced. This is estimated, states *American Vanadium Facts*, 3, No. 4, 3, from the total sales of ferro-vanadium for 1912. Eight years ago the consumption of vanadium steel was practically confined to the automobile and tool steel fields; at the present time its application has been extended throughout the entire field of mechanical construction. In the face of quite drastic retrenchments, the advantages of vanadium steel as a factor making for economy in maintenance has led within the past five years to its extensive employment in locomotive construction.

In 1908, when some railroads specified vanadium steel for test purposes, only 53 locomotives so equipped were built, or only 2 per cent of that year's total locomotive output. From 1910, the increase in the use of vanadium steel for locomotive parts has been steady, and it has been specified for over 730 of the locomotives ordered up to June for 1913 delivery, an increase of 21 per cent over last year's entire output of locomotives equipped with vanadium parts. In 1912, over 25 per cent of the locomotives built weighing over 200,000 pounds were supplied with vanadium steel parts. Tests are now being conducted of heat-treated chrome-vanadium tires, with a view to increasing the greatly diminished tire mileage of the heavy locomotives.

It is said that fully 60 per cent of the 1913 automobiles will contain vanadium steel. Chrome-vanadium steel is also reported to be rapidly supplanting other alloy steels for gears, axles, crank shafts, propeller shafts, jack shafts, rods and springs.

A GERMAN SOOT AND CINDER ARRESTER

Trautmann (*Power*, 37, No. 22, 774) describes one of the successful foreign installations for preventing the soot and cinder nuisance, in operation at the municipal power plant, Pforzheim, Badenia, Germany. Some time ago the increasing demand for electric current required enlarging this plant and erecting a new stack which, out of esthetic consideration for the locality, was carried up only 70 feet high. This made mechanical draft necessary for three new water-tube boilers, each of which has 2375 square feet of heating surface and 65 square feet of grate surface in chain grates. German bitu-

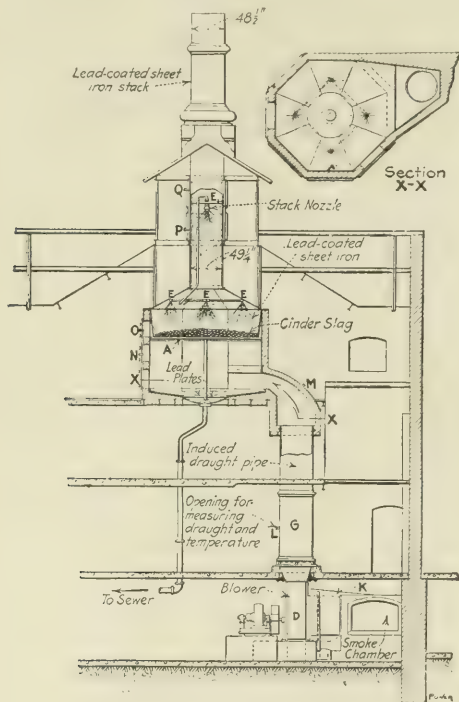


FIG. 1—SECTIONAL ELEVATION. GERMAN SOOT AND CINDER ARRESTER

minous coal is used and the plant has been in successful operation for about five years, the only trouble experienced consisting of a slight fall of condensed steam during times of heavy rainfall. When the boilers are first started the stack discharges a yellow

cloud of steam, but the color soon changes to white as the operation of the plant is continued. Pieces of white cloth placed over the outlet of the stack and kept there for a considerable time during the ordinary running of the plant show only a slightly grayish color without having gathered any particles of soot or cinder.

Fig. 2 is a plan showing the general arrangement of the boiler additions referred to and their draft connections, and Fig. 1 is a sectional elevation showing the induced-draft blowers, stack and cinder catcher. Referring to Fig. 1, B_1 , B_2 and B_3 are the boilers with smoke connections C_1 , C_2 , C_3 , which discharge into the main smoke chamber F .

The exhaust blower D receives the smoke from the boilers

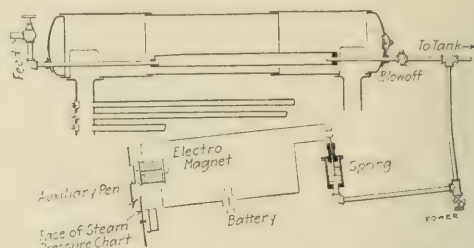


FIG. 2—CONNECTIONS OF BOILER BLOW-DOWN RECORDER

by a short breaching connected with the smoke chamber and forces it into the pipe G , Figs. 1 and 2, from which it passes into the main receiving chamber of the cinder catcher, Fig. 1, which has a cross-sectional area of about twelve times that of the stack. This receiving chamber is of brick, lined on the sides with interchangeable lead-coated sheet-iron plates, while the bottom is covered with lead-coated plates which slope to an opening in the center which is connected to the sewer. Near the top of the chamber is a lead-coated grating, A , for supporting a bed of broken cinder slag, and above the slag bed is a cluster of nozzles, E, E, E , for spraying water as the smoke filters through the bed of slag. A similar cluster of nozzles is provided a little higher up in the stack at E_1 . The slag consists of boiler clinker gathered from the ashes made at the plant, the clinker being broken up to about the size of nut coal and spread over the grating, forming a filter bed 12 to 16 inches thick. The water pressure is made just sufficient to raise the water to the height of the spray nozzles with sufficient pressure at the nozzles to properly atomize the sprays.

When the gases from the boiler furnaces enter the receiving chamber, their velocity is reduced, owing to the enlargement of cross-sectional area, and they part with most of their contained solid matter. Then they filter up the mud drum and then enter the boiler tubes. Although these impurities are mostly what is called soft scale, if they enter the boiler and combine with the scale deposited in the process of evaporation, they will form a hard scale.

While frequent cleaning of the mud drum is desirable, the tendency in the boiler room is to let the matter go and not blow down regularly. An automatic device for recording the time when a boiler is blown off thus gives the engineer a check on the fireman and insures regular blowing down of the boilers.

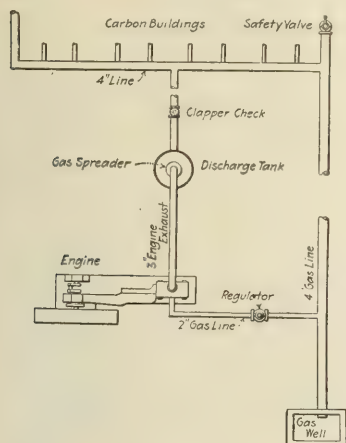
THE MANUFACTURE OF CARBON BLACK FROM NATURAL GAS

An original method of power generation is in operation at the Wilsonburg, W. Va., plant of the Union Gas & Carbon Co., manufacturers of carbon black. The product is obtained from the flames of natural gas by impingement on a smooth surface and final removal of the deposit by means of steel scrapers; it is used in the manufacture of printing ink and paint.

The natural gas is supplied from a well 3000 feet deep and

at a pressure of 950 lbs. Formerly this was led through a 4-inch main direct to the carbon buildings and the power necessary for driving the scrapers, etc., was obtained from a steam boiler and engine.

The management, however, conceived the idea of utilizing the initial pressure of the gas by passing it through the cylinders of the steam engine, the latter serving in the capacity of a reducing valve, and at the same time, doing away with the use



of steam. Accordingly, the piping was arranged as shown in the sketch, a 2-inch branch being taken off the 4-inch gas main and led through a regulating valve to the engine. The exhaust is led into a discharge tank, a spreader being provided at the end of the exhaust pipe. From the discharge tank the gas passes through a 3-inch main to a clapper check valve, which works simulta-

neously with each chug of the exhaust and allows the gas to feed into the carbon buildings with constant regularity.

By using gas in place of steam in this manner, the engine is said to respond quicker and more uniformly. Also, it not only provides free power, but reduces the labor by one man.

A PLANT FOR THE TREATMENT OF IRON PYRITES

The *Iron Trade Review*, June 12, 1913, describes the plant under construction at Roanoke, Va., by the Pyrites Co., Ltd., for the treatment of iron pyrites to render it suitable for blast-furnace use. The company building the plant is associated with the interests controlling the Rio Tinto mines in Spain, which ship pyrites to this country in large quantities, mainly to manufacturers of sulfuric acid. After the ore has been used by these manufacturers, the residue is to be collected at the Norfolk plant, where the copper will be removed and the material sintered for the reclamation of the iron. The sintering is to be carried out in a unit of the Dwight and Lloyd type of 150-ton size. As the pyrites ore contains 60 per cent or over of iron, and the sintered product will run about 0.02 per cent of phosphorus, it is thought that this material will be attractive to blast furnaces in the Virginia and Southern districts. It is planned to enlarge the plant if it proves to be successful commercially.

THE DEPOSITION OF NICKEL

The depositing of nickel in thick layers has been a difficult problem to solve, because of the tendency of this metal to raise up and peel off. In fact, the layer of nickel exercises considerable pressure on the conductor that it covers and has a tendency to detach the metal already deposited. The cause of this exfoliation is, according to the *Chemical News*, 107, 294, probably the hydrogen which is discharged at the cathode at the same time as the nickel is deposited. In the presence of much hydrogen, the metal forms a pulverulent deposit; if the gas is less abundant, the nickel becomes saturated with it, loses its suppleness, and peels off.

It is well known that nickel in thick layers presents decided advantages over certain other metals; among other applica-

tions, it would, in particular, permit of the manufacture of printing clichés which would be practically everlasting. Recently Hollard has endeavored to obviate the objectionable hydrogen, by conducting the electrolysis with a complex combination which gives out hydrogen with difficulty. He has employed nickel fluoroborate, which gives excellent results for an intensity of current of 1 ampere for electrodes 14×18 cm. at a distance of about 4 cm. in a solution possessing a density of about 1.08. This bath is said to deposit the nickel directly on cast-iron and on aluminum.

TUNGSTEN FILAMENT LAMPS

An editorial discussion of the recent report on tests of tungsten filament lamps made by the British Engineering Standards Committee appears in the *London Electrician* for June 6, 1913.

The lamps tested were those on the market some eighteen months ago and showed great improvements over the older lamps but left much to be desired with respect to rating. The objects of the tests were to obtain data as to the degree of uniformity in the individual lamps composing batches of metallic filament lamps of given nominal ratings, and also to obtain data as to the behavior of metallic filament lamps on life tests, with a view to ascertaining the value of the watts per candle-power on life tests which correspond to a given candle-power drop after 1000 hours. The lamps were assumed to have been manufactured to conform to the values of watts and candle-power which were advertised in the respective makers' catalogs for the rating in question. From the target diagrams and tables it appears that "individual lamps on the market at that time, with the exception of those of one maker, vary considerably from their normal ratings, while even that maker whose lamps do not so vary cannot flatter himself exceedingly, as the lamps in question were supplied to a government department, a type of consumer that is, as is well known, extremely rigorous with its lamp-testing, so that these particular lamps can hardly be considered an ordinary works product. As regards the results of the candle-power tests, only 40 per cent of the batches tested came within the percentage limits laid down by the carbon-lamp specification and the same percentage within the makers' suggested limits. On the wattage basis the percentages complying with the two specifications were 48 and 79, respectively." The percentage-limit described in the British standard specifications for carbon lamps is $\pm 12\frac{1}{2}$ per cent for candle-power and ± 8 per cent for watts. Life tests were conducted on a basis of 1.2 watts per c.p.—that is, the voltage was found at which each lamp consumed 1.2 watts per c.p. and the lamp was then run at this voltage for 1000 hours or until it broke. Lamps with a life of several thousand hours are exceptional. "Moreover, the percentage of lamps which do not exist even for 1000 hours is higher than would be believed, especially in the case of high-voltage lamps. The candle-power throughout, however, seems to remain sufficiently constant to be satisfactory, and this statement applies equally to both high-voltage and low-voltage lamps."

THE PLATINUM MARKET

During June, 1913, business was rather quiet, although steady, and prices remained firm at \$45 to \$46 for refined platinum, and \$49 to \$52 per ounce for hard metal. It was reported from Russia in the end of June that there was no material change in the market; prices equivalent to \$36.66 at Ekaterinberg and \$37.04 at St. Petersburg were quoted for crude metal, 83 per cent platinum, per ounce. Small quantities only were offered by the starateli, and these were quickly taken up by speculators; it was said that an advance in price was expected. At this time, several companies were being organized to lease tracts of platinumiferous gravels, and to operate, on a good scale, with modern appliances.

With regard to the iridium market, it may be said that no increment in supplies was apparent in June, 1913; accordingly, the price remained high, \$85 per ounce in New York. There was some disappointment expressed that the reported discovery of a large discovery of osmiridium in Tasmania was in doubt; it appeared from reports that much further development was required and that, up until then, only a few small pockets of ore had been found.

THE MANUFACTURE OF SALT

In 1908, J. Hodgkinson, of Manchester, England, devised an apparatus for evaporating brine for the production of salt. This was adopted by the Commercial Salt Company, Ltd., which firm has operated the Hodgkinson process at its Cheshire plant for four years. A primary closed evaporating tank is heated by a furnace fed by an automatic stoker which distributes the fuel over the fire-bars, so as to maintain a constant temperature. The furnace is arranged adjacent to the pan, but not directly beneath it; in this way the flames do not come into direct contact with the base of the evaporator. The tank is provided with a rotary scraping device for removing the product and also with a paddle for breaking up surface films. The steam from the primary tank is conducted under the false bottom of a secondary closed evaporator, being superheated by the partially spent furnace gases. The product may be similarly removed from this evaporator, and the steam from it, superheated by the furnace gases, is used to heat auxiliary open tanks, the gases then passing on to heat a further series of open tanks which may be heated also by exhaust steam. Heated brine is fed into the evaporating pans, and there are means for inducing the flow of gases through the flues, which are provided below the evaporators with baffles for the uniform distribution of the heat. It is claimed that owing to the uniformity of temperature, the primary pan produces continuously the same quality of fine salt, and that salt of uniform, though coarser quality, is obtained from the auxiliary pans, that from the last series of open tanks at the lowest temperature being the coarsest.

According to Wallen,¹ the Hodgkinson salt-making process is superior to any other known method of making salt. The revolutionizing feature of the process is that it produces an absolutely uniform crystal, finer than the finest ground salt and free from the dust which is inseparable from salt obtained by grinding. Over five tons of salt may be produced from the combustion of one ton of coal; at the same time and in one operation, every grade or variety of salt for domestic, dairy and fishery purposes may be manufactured. Moreover, by the mechanical regulation of the heat the plant can be made to produce any given quantity of the particular grade of salt to meet the current market requirements. A comparison of leading methods showed that while the Salt Union's "vacuum process" made salt for about \$1.92 per ton and the International Salt Company claimed to be able to produce salt by their system of treating rock salt at \$1.36 per ton, the inclusive cost of manufacturing salt by the Hodgkinson process is said to be under \$0.84 per ton. Wallen stated that the Commercial Salt Company, Ltd., has acquired some of the best brine land in Cheshire, England, and that the works should very shortly be in a position to produce 1,000 tons of salt per week.

Commenting on the report of Wallen, it is noted editorially in *The Chemical Trade Journal*, 52, 622, that in some quarters there seems to be some misapprehension as to the cost of making salt in the old open pans and by the vacuum process. The open pans will make anything from 36 to 40 cwt. of salt per ton of slack, and an efficient vacuum installation is able to make 5 tons of salt for every ton of slack consumed, besides which a large amount of power can be made available at a low cost. "The total cost of manufacture by the Hodgkinson process

was stated to be \$0.84 per ton. . . . If this is the best the process can do, the margin over the other processes will not be anything like so much as the shareholders will anticipate from their chairman's (Wallen's) statement. The chairman made the further statement that the salt produced by the vacuum process was not suitable for table use, but had to be ground . . . vacuum salt can be produced in very small crystals, and is quite suitable for table use."

PROPOSED DEVELOPMENT OF AMERICAN POTASH DEPOSITS

A company—the American Trona Company—has been organized, with a capital stock of \$3,000,000, to develop the deposits of potassium salts at Searles Lake, near Death Valley, California. Another organization—the Nevada Potash Company, Goldfield, Nevada—plans the development of a reported potash deposit in Clayton Lake, 20 miles west of Goldfield; it is reported that the company will commence experimental work immediately on the 160 acres controlled. The large deposits of alunite near Marysville, Utah, are controlled by the Florence Mining and Milling Company, of Philadelphia, Pa.

THE FERTILIZER INDUSTRY OF CHARLESTON, S. C.

Hanahan (*Am. Fertilizer*, 38, No. 13, 52) points out that the industry of manufacturing fertilizers may be rightly said to have originated and received its first development in Charleston, S. C., where the following plants are now in operation:

Planters' Fertilizer and Phosphate Company.
Interstate Chemical Corporation.
Ashepoo Fertilizer Company.
Atlantic Phosphate Company.
Chicora Fertilizer Company.
Imperial Fertilizer Company.
Macmurphy Company.
Standard Fertilizer Company.
Etiwan Fertilizer Company.
Combahee Fertilizer Company.
Read Phosphate Company.
Wulbern Fertilizer Company.
Virginia-Carolina Chemical Company.

The value of fertilizers consumed in the South has increased from \$29,277,000 in 1900 to \$84,635,229 in 1912, or over 290 per cent in twelve years. In this expansion of business Charleston has held her own trade fairly well, and remains the largest producing point of sulfuric acid (about 175,000 tons per year). In 1912, 535,023 tons of manufactured fertilizers and fertilizer materials were shipped out of Charleston by railroad; the shipments for 1913, up to April 15th, amounted to 407,320 tons. The total South Carolina tax tags sales, valued at 25 cents per ton, were \$221,555.75 (886,223 tons) in 1912. The imports of fertilizer materials into Charleston were valued at \$3,805,699 in 1912.

There are three large phosphate rock mines in operation in South Carolina, viz.: Charleston, S. C., Mining and Manufacturing Company; Bolton Mines; and Bulow Mines. Owing to their greater contents of phosphoric rock and cheaper cost of mining, the phosphate rocks of Florida and Tennessee have gradually driven the South Carolina rock from all markets except the local and coastwise ones.

THE CONSUMPTION OF VARIOUS NITROGEN-FERTILIZERS IN AUSTRIA

Die Chemische Industrie, 36, 352, reports that with the increase in price of Chili saltpeter and ammonium sulfate, the consumption of calcium cyanamide and Norway saltpeter has appeared to increase in Austria since April 1, 1913. Norway saltpeter is a duty-free article and cheap freight rates are offered for its transportation. In 1912, Austria consumed only 1,500 tons of

¹ *Chem. Trade J.*, 52, 632.

Norway saltpeter, while the 1913 consumption is estimated to be 3,000 to 4,000 tons. The production of calcium cyanamide by the *Società Anonima Per La Utilizzazione Delle Forze Idrauliche Della Dalmazia* in Sebenico has so far amounted to about 6,000 tons; it is thought, however, that this output will be considerably increased when the works at Almissa are completed. In 1912, Austria consumed 5,000 tons of calcium cyanamide; the results obtained from its employment were not altogether unfavorable and no complaints were made concerning the difficulties which were encountered upon its introduction.

The question for the future of the calcium cyanamide industry seems to be whether it will be possible to ensure the demand when the price of Chili saltpeter falls. There is no doubt, however, that, for a number of years, either Norway saltpeter or calcium cyanamide will determine the price of Chili saltpeter and ammonium sulfate.

THE GAS INDUSTRY OF ENGLAND

Elliott (*Am. Gas Light J.*, 98, No. 26, 420) states that about 1850 there were some 13 gas companies in England, operating works within a radius of 4 miles from Charing Cross and having a total capital of about \$25,000,000. These works contained retorts, with about 10,000 mouthpieces, and used about 800,000 tons of coal to produce 8 thousand million cubic feet of gas per year. The price of gas was 6 to 7 shillings (\$1.50 to \$1.75) per 1,000 cubic feet. All the companies were competing for business, and were not very happy in the matter of paying dividends. It was estimated that at least one-ninth of the gas made did not reach the consumers, the leakage from the mains being so high. The residuals (principally coke and some tar) brought a return of about \$3,000,000 per annum. About 13 gallons of ammoniacal liquor of 4° Twaddle (8 ounces) was the average yield per ton of coal carbonized. This liquor was sold for about 2 shillings 7 pence (40 cents per butt: = about 130 gallons). The average yield of tar was about 11 gallons per ton of coal carbonized. Comparing these figures with the results of recent times, the value of the tar has become much more important, because, at that time, there was no aniline color industry.

The principal uses of tar were as a wood preservative, for covering iron, and for some sorts of wooden work, especially fence posts and rails. Some naphthas were obtained by distillation, for making varnishes, and for burning in lamps, and the green oil, which distilled off last, was used for axle grease. This material was afterward (1870) found to yield anthracene that gave the beautiful turkey-red dye, and revolutionized the Dutch madder industry.

The various London companies were in keen competition for business when another competitor entered the field with a challenge of four shilling gas, and a promise of further reduction. This new company was the Great Central Gas Consumers' Company, engineered by Alexander Angus Croll, and the president of the company was Mr. Dakin, the tea merchant. The works were calculated to produce 800 million cubic feet per annum, and cost £210,000 (\$1,050,000) with 4 gasholders of a capacity of 1,000,000 cubic feet. The company laid 70 miles of mains and the output was about 100,000 cubic feet per day, produced from 10 or 11 tons of coal. Mr. Croll was interested in an alum works, in which he, no doubt, used the ammoniacal liquor of the gas works. He was also the inventor of improvements in gas meters, and had a meter manufactured in London. Like all enterprises of this character, the Great Central Gas Consumers' Company was ultimately absorbed (1870) into the Gas Light and Coke Company. By way of contrast, compare the English gas industry of to-day, with its output of over 200,000,000,000 cubic feet per annum. Of this, the great Bechtow works can produce 60,000,000 cubic feet per day, and uses 1,000,000 tons of coal per annum. The South Metropolitan works and the Commercial Company's plant will probably produce as much more.

The consumption of gas per capita of population per annum is now over 8,000 cubic feet, and it is calculated that only 10 per cent of this is used for illumination in flat flame burners. Compare also the value of the residuals with that of 50 years ago. The yield of tar per ton of English coal is about 13 gallons; and of ammoniacal liquor about 40 gallons of 8 ounces strength. In addition to this, some works now recover cyanogen, which was formerly lost in the iron mass used for purification.

THE PURIFICATION OF COAL GAS

In an address delivered before the Institution of Gas Engineers, June, 1913, W. B. Davidson dealt with the removal of the impurities present in crude coal gas from a commercial and practical standpoint (*Chem. Trade J.*, 52, 679).

The valuable and complex product, tar, worth from \$0.84 to \$1.68 per ton of coal carbonized, contained many different compounds—nearly 200 of which had already been identified. Vertical retort installations had not hitherto been designed to reduce as successfully to a minimum the cost of tar handling as the old installations of horizontal and inclined retorts, though he was of the opinion that the working could be made just as easy as with the horizontal systems by circulating hot water through the hydraulic main and providing agitators for mixing the contents of the same before running off. When the hydraulic main was very hot, as with coke ovens and some vertical retorts, ammonium chloride showed itself in the form of small crystals which rendered the tar less fluid and gave rise to stoppages in the tar pipes. A remedy for this was the introduction of water or liquor in the hydraulic main at definite intervals, preferably before agitating and drawing off the contents. There were two ways in which losses might be sustained by the gas manufacturer if he did not look carefully after tar removal. One was in the large amount of benzene which might be extracted by tar by too drastic condensation or prolonged contact with the gas, and the other was the degree of freedom of the gas from the last traces of tar before entering the ammonia washers. The presence of even a few grains of tar per 100 cubic feet was sufficient to render ammonia washers liable to get blocked up.

Naphthalene would be a valuable ingredient as regards both candle power and calorific value were it not that it is prone to condense out in the solid state in awkward situations, or were it not volatile at high temperatures. As it was, it could be regarded only as an impurity. It was most prevalent in gas made in horizontal or inclined retorts at high temperature or with light charges. It was not so much the quantity of naphthalene present that determined the necessity of purification as the proportion of vapor of heavy oils which condensed out along with the naphthalene and kept it in solution. This impurity offered comparatively little difficulty when suitable preventive measures were employed.

The content of hydrocyanic acid in crude coal gas amounted as a rule to only 0.22 per cent by volume, which, converted into crystals of prussiate of soda, was equivalent to 4½ lbs. per 10,000 cubic feet, or 5.4 lbs. per ton of coal. The elimination of hydrocyanic acid from coal gas was optional, but in any case the great bulk of it would be removed by the iron oxide in the ordinary purifier with formation of Prussian blue; but for the sake of improved purity, and the prevention of corrosion and stoppages, it was very desirable that it should be removed as completely as possible.

During past years, until just recently, there had been small incentive to extract cyanogen for sale, owing to the low price of prussiate of soda. Recently prices had shown an upward tendency, and it was possible on a large plant to make a net profit of about \$0.02 per lb. of prussiate of soda recovered per ton of coal.

Davidson believed that a great deal of laxity prevailed generally in the estimation of sulfuretted hydrogen. Concern as

to the quantity present was lessened by the fact that purification with oxide of iron was a very simple process; and, moreover, exact methods of determination were rather troublesome. With proper precautions the ordinary absorption method of gas analysis could be applied with success, especially for purposes of comparison. Midland coals yielded on an average 1.4 per cent of sulfuretted hydrogen in the crude gas, which was equivalent to 14 lbs. of sulfur per ton of coal.

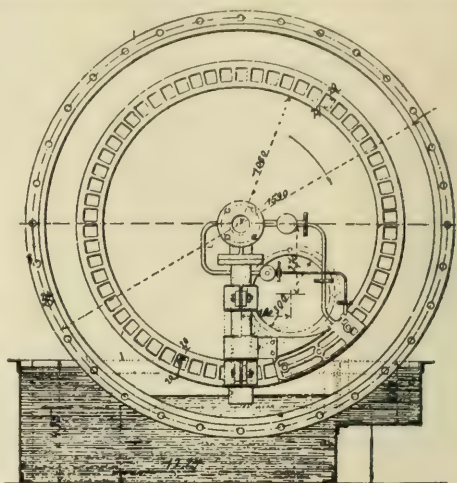
Davidson discussed the utility of ammonia as a purifying agent. To members of the Birmingham gas engineering staff it became clear some years ago that Young, Hills, Claus, Holgate, and others in the sixties and subsequent years had not discovered the true science and art of distilling gas liquor. The large scale experiments on the Claus process carried out at Belfast failed very badly; not only was the elimination of sulfuretted hydrogen and carbonic acid very incomplete (about 50 per cent), but the losses of ammonia were so great as to be fatal to any process of the kind. During the past few years Davidson had carried out a large number of experiments both in distilling and in gas washing in the works and in the laboratory, with results sufficiently promising to convince the Birmingham Gas Committee that something could be done on similar lines to those of the Claus process, but with important improvements in the methods of distilling the liquor and washing the gas.

About two years ago the erection of a liquid purification plant was started on the coal-test plant for the treatment of the gas made by the test installation of 18 Dessau retorts carbonizing 14 to 16 tons of coal daily. The plant included a still, condensers, sulfur kiln, and depositing chambers, with the necessary tanks for storage of liquor. With the object of carrying out preliminary tests an additional gas washer of the vertical centrifugal type, together with a simple tower scrubber, had been provided a year previously, and after twelve months' trial—not quite continuous—the process of extracting sulfuretted hydrogen and carbonic acid from the gas by means of purified ammonia solution had been pronounced successful, and the plant was now being enlarged and improved so as to deal with twice the amount of gas.

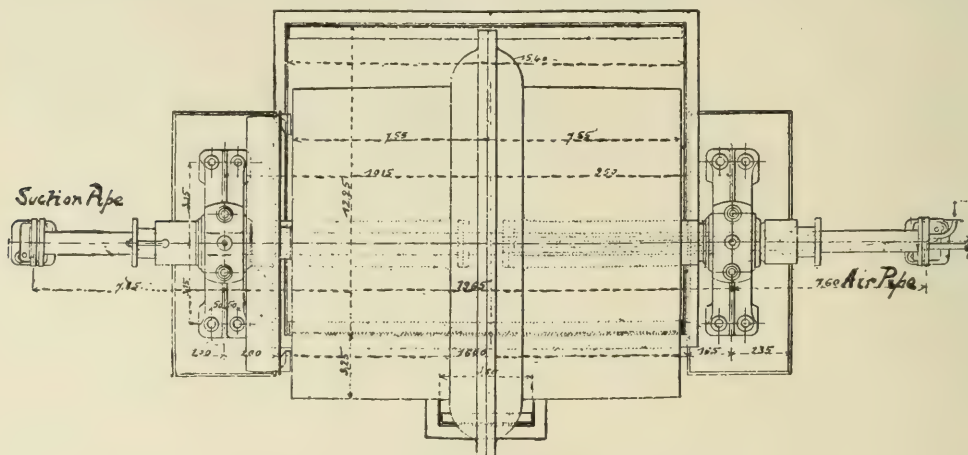
THE MANUFACTURE OF GAS FROM SEWAGE SLUDGE

According to the *American Gas Light Journal*, 98, No. 23, 367, a process has been adopted by the Municipality of Brunn, in Austria, by which the solid matter in sewage is transformed

It has been found necessary to have a powerful filtering apparatus of large output, and for this purpose Abt & Bayer have constructed the continuous filtering machine, illustrated in the figures shown herewith, which are taken from a paper on the subject read by Leonce Fabre, before the Société Technique de l'Industrie du Gaz en France. The machine consists of a cylin-



drical drum, the surface of which is formed of long filter cells parallel to the axis, the cells being so arranged that they dip into the tank or chamber containing the sewage mud. On the inside they are connected to a centrally situated chamber, common to all, in which a vacuum is produced, as described below. The hollow shaft supporting the system of cells forming the drum is arranged to permit the rotating of the machine. One end of the shaft carries a pipe to the inside of the chamber, turning down into the central chamber, and immersed in the filtered liquid in its lowest portion. The pipe which is connected to a suction pump assists the action of the filtering cells, and extracts a large amount of moisture from the filtered material as the drum revolves. In the other end of the shaft there is another tube, which carries compressed air to the inner surface



into gas, economically and successfully. The apparatus is to be used effects the drying of the sewage matter, and this dried material is afterwards distilled in retorts in precisely the way that coal is treated.

of each cell in rotation, the point at which it is brought under the action of the compressed air being shown in the transverse section. The drum is rotated slowly, and each cell filled with the dried material comes in turn to the point where the vacuum

ceases, and passes under the influence of the compressed air, which, acting on the interior of the cell, dislodges the material from the filtering diaphragm in the cell being treated; and this solid material from the filtering process, after being thus partially dried, is taken away for the subsequent coking and gasifying process.

The water withdrawn by the suction pump is always clear; the necessary motive power is quite small, and the dried material is obtained in the form of cakes or plates 2 or 3 mm. thick, a convenient form for further drying. The drum has a useful filtering surface of 25 square mm. divided into 60 cells. The vacuum acts on 55 of these cells at a time, while the compressed air acts on a cell at a time. Experience has shown that the distillation of the damp material, when used without the addition of coal, does not give as good results, either from the point of view of the calorific power of the gas obtained or of the ammoniacal residue, etc., as when dry material is used. It is, therefore, necessary to dry the caked material obtained from the rotary filter, using any of the various well-known types of drier, before gasification in retorts similar to those used in ordinary gas making with coal. It has been found that, after $2\frac{1}{2}$ hours of distillation, 100 kg. of sewage mud yields 23.8 cubic cm. of gas, of practically the same composition as that obtained from coal, and the coke yield is of good quality and consistency; while, as regards ammonia, three times as much is obtained as that usually yielded by an equal weight of coal. It is stated that, in addition to the value of the process in disposing of the sewage in a convenient and hygienic manner, the actual profit obtained from its operation has been found sufficient to pay for the gas for working the purification process. It is, therefore, an interesting development in modern sewage disposal practice, the future progress of which will be followed with interest by the authorities of many populous centers.

THE CAUCASIAN PETROLEUM INDUSTRY

While obviously continuing to decline in prosperity, owing to the systematic exhaustion of its long-drained oil fields, the activity of the Baku oil industry was, nevertheless, very marked during 1912 (*Oil and Color Trades J.*, 43, No. 766, 2173). The prices of oil reached record figures during the year, and these

prices were accompanied by an increase in production, owing to the greater activity exhibited by producers in boring new wells. The crude oil produced amounted to about 7,725,000 tons as against about 7,516,000 tons in 1911. The total yield from new wells was about 890,322 tons.

On the other hand, despite the increase in production, the petroleum consuming markets of Russia experienced a very great scarcity of oil throughout the year, and many consumers of liquid fuel were compelled to fall back on coal for fuel purposes—a very expensive measure, in view of the coal famine experienced throughout Russia during 1912. The exports of petroleum products from Batoum show a decrease of 49,546 tons on the 1911 figures.

THE CONDITION OF THE SCOTTISH SHALE OIL INDUSTRY

The position of the Scottish shale oil companies at present is as follows:

Name of company	Net profit, 1913, in pounds	Dividend on ordinary shares Per cent.	Placed to depreciation, in pounds
Young's.....	88,861	5	20,000
Pumpherson and Tar- brax.....	151,935	35	15,000
Oakbank.....	56,847	15	12,000
Broxburn.....	73,705	10	15,952

All the companies are reported to have ample reserve funds for new retorts and additions to refineries. The large Pumpherson Company, which took over the Tarbrax Company during 1912, has just had extensions made to its works at Pumpherson, Mid-Calder, and plans to extend its crude oil works at Seafield; all the crude oil from the plants at Tarbrax, Seafield and Deans is conveyed by railway to the refinery at Pumpherson, which covers 100 acres. The paraffin section of the refinery is now undergoing development. New shale fields are being opened and the electrical power plant is of the latest type at all the Scottish works. Operating costs are high, but profits are constantly being increased by adding to the output; it is said that present prices will be maintained. At the Young's works a cascade plant is to be erected in lieu of the present vitriol bottle house, and about \$30,000 has been laid out recently on the replacement of vitriol chambers.

SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY—ROCHESTER MEETING

The forty-eighth annual meeting of the American Chemical Society will be held in Rochester, New York, September 9th to 13th, inclusive. A meeting of the Council will be held on Monday night, September 8th, at the Hotel Seneca, immediately following the complimentary dinner to be given to the Council at seven o'clock.

The program will open with a general meeting on Tuesday at 10 A.M., in the assembly hall at Kodak Park. Members should make a special effort to be present at this opening meeting, as it will not only be one of the most interesting meetings of the session, owing to the fact that it will contain the general addresses, but the whole day will be one of special features, inasmuch as the members of the Society are to be the guests of the Eastman Kodak Company at luncheon following the morning meeting, and the afternoon will be spent in visiting the immense plant of the Eastman Kodak Company at Kodak Park. This will be the only opportunity to visit the Eastman Kodak Company. As the company is making special efforts to entertain the membership, it is hoped that every member will endeavor to be present at this first session.

There are already signs that the meeting this September will be the largest that the Society has ever held as a separate

organization, and it is probable that from 700 to 1000 chemists will be present. All divisions will meet; and the biological section will be duly organized as a division, electing its officers on Friday morning.

A smoker will be held at 8.30 P.M., Tuesday, in Masonic Hall. The divisional meetings on Wednesday, all day, and Thursday and Friday mornings, will be held in the Eastman Building, University of Rochester. The President's address will be given at the East High School, Rochester, at 8 P.M., Wednesday; and the subscription banquet, Thursday night, at 7 P.M., at Powers' Hotel.

On Thursday and Friday afternoons excursions will be open to the following manufacturing plants: Bausch & Lomb Optical Co., Taylor Instrument Co., Curtice Bros. Co., J. Hungerford Smith Co., Moerback Brewery, German-American Button Co., Genessee Reduction Co., Municipal Incinerator, Stecker Lithographic Co., and possibly others.

The local committee is made up as follows:

GENERAL: V. J. Chambers, F. R. Baxter, H. E. Howe, Harry LeB. Gray, J. O. Schlatterbeck, Ernest Little, J. E. Woodland, and the following chairmen of sub-committees: *Finance*, F. W. Lovejoy; *Registration and Information*, H. A. Carpenter; *Arrangements*, Ernest Little; *Press*, A. E. Crockett; *Banquet*,

C. F. Hutchinson: *Entertainment*, M. H. Eisenhardt: *Ladies*, Miss Lattimore: *Factory Excursions*, J. E. Woodland: *Vacation and Side Trip*, H. LeB. Gray.

PAPERS FOR MEETING

All papers for the meeting must be in the Secretary's hands on or before August 22, or in the hands of secretaries of divisions by August 20, in order to be on the program. Especially the secretary of the Organic division requests that organic papers be sent direct to him. By vote of the Council, no papers can be presented at the meeting that are not printed on the final program. The following are the addresses of the divisional and sectional secretaries:

AGRICULTURAL AND FOOD—G. F. Mason, care of Heinz Company, Pittsburgh, Pa.

BIOLOGICAL—I. K. Phelps, Bureau of Mines, 40th and Butler Sts., Pittsburgh, Pa.

FERTILIZER—J. E. Breckenridge, Carteret, N. J.

INDUSTRIAL—S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa.

ORGANIC—Win. J. Hale, University of Michigan, Ann Arbor, Mich.

PHARMACEUTICAL—Frank R. Eldred, 3325 Kenwood Ave., Indianapolis, Ind.

PHYSICAL AND INORGANIC—R. C. Wells, U. S. Geological Survey, Washington, D. C.

RUBBER—Dorris Whipple, care of the Safety Insulated Wire & Cable Company, Bayonne, N. J.

WATER, SEWERAGE AND SANITATION—Edward Bartow, University of Illinois, Urbana, Ill.

Apparatus and materials will be supplied to those wishing them for demonstration purposes. It is particularly important that the Secretary be informed of any papers requiring a lantern for their illustration.

VACATION AND SIDE-TRIP COMMITTEE

Attention is called to a new committee in connection with our next meeting in Rochester, namely, a Vacation and Side-Trip committee, whose object is to furnish information to those desiring it relative to train and boat connections in and out of Rochester and automobile trips. The committee desires to call attention to the Canadian National Exhibition at Toronto, August 23 to September 9. It is of the utmost importance that those intending to visit the Exhibition in connection with the Rochester meeting secure accommodations in Toronto at the earliest possible time. Full information can be supplied by this committee. Address H. LeB. Gray, Eastman Kodak Co., Rochester, N. Y.

FINAL PROGRAM

The final program will be sent to all members of the Rochester Section, to secretaries of local sections, to members of the Council, and to all members who make special request thereof by postal card to this office. The expense of printing and mailing this program is so great that it will be sent only to those who especially desire it on account of their intention of attending the meeting. Other members will find it printed in the Society's journals.

ABSTRACTS OF PAPERS

Abstracts of papers should be prepared and brought to the meeting, or, even better, sent to the Secretary in advance thereof. Members sometimes fail to realize how important this is to the success of the Society and to the proper advertisement of the meeting itself. Unless abstracts of the papers are brought to the meeting and early placed in the Secretary's hands, there is no opportunity for proper publicity in the local press, which is of very great advantage to the Society. Members will greatly aid the Secretary's office by remembering this fact.

HOTELS

The Hotel Seneca has been selected by the local committee

as headquarters. It is essential that accommodations for the meeting should be secured at the earliest possible moment, as another convention is to be held in Rochester during the week of September 8, and members of the Society coming without previously having secured rooms may be seriously inconvenienced.

ENTERTAINMENT OF VISITING LADIES

During recent meetings, and especially at the annual meeting, the number of visiting ladies has tended to increase; and it is hoped that many of the members will bring ladies with them to the Rochester meeting. Every effort will be made to make their stay in Rochester an enjoyable one, and the local committee has outlined the following additional entertainment for the ladies who are present:

TUESDAY, September 9, 8.30 P.M., Card Party, Century Club.

WEDNESDAY, September 10, 10 A.M., Complimentary Excursion to Irondequoit Bay and Luncheon at the Newport House: full day trip.

THURSDAY, September 11, 9 A.M., Auto Excursion of 45 miles about parks and Irondequoit gardens.

INDUSTRIAL DIVISION ANNOUNCEMENT

The secretary of the Industrial Division, Mr. S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa., wishes to announce that a new descriptive directory of the division will probably be issued the latter part of this year, provided members do their part toward its preparation and publication. In order that the directory may be a success, it is necessary for all members engaged in industrial work who are, or who wish to be, registered in the Industrial Division, to send to Mr. Salisbury their present address and the occupation in which they are engaged, together with the lines of industrial chemistry in which they are most interested. It is also very essential that this information be accompanied by a contribution of \$1.00 toward the expenses of the division and the publication of the directory.

It is hoped that members will endeavor to arrange their summer vacations so that they can be present at the Rochester meeting, which is certain to be one of the most enjoyable ever held by this Society.

CHARLES L. PARSONS, *Secretary*

Box 505, WASHINGTON, D. C.

NEW SECTION ON WATER, SEWERAGE AND SANITATION AT ROCHESTER MEETING

At the last meeting of the Council in Milwaukee Dr. Edward Bartow was asked to sound members of the Society as to their desirability of forming a new section on Water, Sewerage and Sanitation. Professor Bartow has already received 52 replies from members who state their interest in the formation of a section, 24 of whom will be present at the Rochester meeting, and he has also received a promise of thirteen papers.

Accordingly, a meeting of this section will be held in Rochester and any others desiring to take part in the program should address Professor Edward Bartow, University of Illinois, Urbana, Ill., sending titles of papers before August 20th.

THE ANNUAL CONVENTION OF THE AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS

Several papers of interest to the chemical engineer were presented at the annual convention of the American Institute of Electrical Engineers, held at Cooperstown, N. Y., June 23 to 27, 1913. The abstracts which follow are taken from the *Electrical World*, July 5, 1913, p. 15.

McClellan deplored the lack of a united engineering profession, and proposed the formation of a general engineering society, to be known as the American Engineering Association, which would include no personal memberships, but in which the present national engineering societies would participate by electing representatives annually. No business or trade

organizations would be included. According to McClellan, the present lack of unity has prevented the engineering profession from exerting its proper influence in the solution of economic problems and has also prevented the profession from having the standing it deserves among the learned professions. Among the functions of such a general engineering society as that proposed would be arrangement of an annual convention for the discussion of engineering in general, the holding of semi-annual meetings, investigation of various subjects, appearance in national and civic matters, etc. To carry such a scheme into effect, it should have the support of at least three of the national engineering societies.

In the discussion of McClellan's paper, Mailloux characterized it as one of the most interesting contributions presented before the Institute in a long time. This, he said, is one of the means of raising the status of the engineering profession; the proposal should, therefore, be fostered and promoted. Oberlin Smith indorsed the proposal, but felt that too much clannishness among members of different national engineering organizations exists to make the project feasible just yet. The civil engineers, he continued, still consider that their society represents all the domain of engineering except military engineering, although there is a growing sentiment among many of them for a united national society. C. L. Clarke, who indorsed the plan of McClellan, urged that clannishness would be no obstacle to its accomplishment, because none of the functions of any of the constituent societies would be disturbed. D. C. Jackson and C. L. de Muralt also indorsed the plan.

In a paper by Burton McCollum and K. H. Logan was discussed generally the subject of electrolytic corrosion of buried iron from outside current sources as well as from self-corrosion within the piece itself. The two actions are to a large extent interdependent, the existence of one affecting largely the occurrence or severity of the other. In the tables of experimental data compiled by the authors the factors are given which are most likely to effect electrolytic corrosion of buried pipes under practical conditions. Among these elements are current density of discharge, moisture content of the soil, presence of oxygen, temperature, voltage, etc. In the laboratory tests carefully cleaned iron anodes were tested in cans of sifted earth moistened with distilled water. Meanwhile, check specimens of iron were also embedded in protected sections to investigate simple self-corrosion. Detailed precautions were necessary in the preparation and cleaning of the specimens. To afford a variety of practical conditions, soils from various localities were used in the tests. The authors discussed briefly earth resistance, polarization and surface-film resistance, presenting tables

of results of specific resistance and corrosion tests, etc. A number of practical conclusions were drawn from the experiments, it being found, among other facts, that corrosion is most efficient at low current densities and is independent of temperature, of depth of burial and of the oxygen present in electrolytes. Soil resistance varies with moisture content up to the point of saturation.

Information of interest to the industrial power engineer was given in a paper by C. A. Kelsey outlining the principal operations in the process of working up raw rubber. This material has a large capacity for absorbing power and is greatly improved by such working. Motor drive of sheet rolls involves an irregular load with abrupt peaks. Mixing, masticating, tubing, calendaring, etc., are some of the other operations involving special applications of motors. Certain operations of "working" and mixing also have heavy overloads of short duration, but these diverse demands, by grouping under a single motor, result in reduced peaks. For individual drive, squirrel-cage induction motors are preferable. In the calendaring processes where close speed control over ranges of four to one is required, direct-current motors may be used to advantage, speed adjustments being effected by the multi-voltage and adjustable-voltage methods. The tubers also require direct-current operation. As the power required to drive the mills is by far the greatest part of the total requirements, alternating-current service is generally selected. The motor-generator set or synchronous converter used to supply direct current can then be used for power-factor correction of the main circuit. In conclusion, there was given a comparison of methods for obtaining adjustable-speed operation, with emphasis on the features to be embodied in the control.

INTERNATIONAL ASSOCIATION OF CHEMICAL SOCIETIES

Monsieur Ernest Solvay, of Brussels, has intimated his intention to place at the disposal of the International Association of Chemical Societies a sum of nearly a million francs for the purposes of the Association, together with rooms in his Institute in Brussels.

Prominent members of the Association suggested that it would be fitting that its meeting in September should take place in Brussels instead of in London, in order that the members present may have an opportunity of conveying their thanks personally to Monsieur Solvay for his munificent gift.

The next meeting of the International Association of Chemical Societies will, therefore, be held in Brussels, beginning September 19, 1913.

NOTES AND CORRESPONDENCE

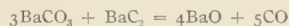
GERMAN MANUFACTURE OF BARIUM COMPOUNDS

Consul Thomas H. Norton reports that until recently heavy spar—barium sulfate—served almost exclusively in Germany as raw material for the manufacture of barium oxide, barium hydrate, barium peroxide, and the various salts of barium. The sulfate was reduced by heating with coal in kilns to the form of the sulfide. From the solutions of the latter, barium carbonate was precipitated by the action of carbon dioxide. This carbonate served as the starting point for the preparation of the chloride, the nitrate, the oxide, etc.

It has now been found possible by the process of W. Feld (German Patent No. 149,803, of 1901) to reduce directly natural barium carbonate (witherite) to the form of oxide by heating in retorts in the presence of a fuel free from hydrogen. The cheap witherite of England is now imported in considerable quantities into Germany to serve this purpose. The import

amounts annually to about 450 metric tons, valued at \$16.65 per ton.

Several other methods have been patented in Germany, but it is not known to what extent they have been introduced as technical operations. A. Frank patented in 1901 (German Patent No. 135,330) a process based upon the interaction between barium carbide and barium carbonate when mixed and heated:



There is a vigorous evolution of gas, and when this ceases the reaction is complete.

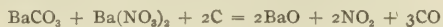
H. Schulze, of Bernburg (German Patent No. 240,267, of 1907), finds it possible to secure a very porous form of barium oxide by the direct reduction of the carbonate, if the retort employed for the purpose is lined with carbon, and if a narrow space is left free between the walls of the retort and the mixture of carbonate and coal. Otherwise, compact crusts are formed

adjacent to the walls and particles of coal are inclosed in them. In a patent of later date (German Patent No. 231,645, of 1909) this inventor describes an additional method of effecting the reduction of the carbonate with coal. Use is made of an electric furnace, and the mixture of mineral and coal is exposed to combined electrothermal and electrolytic action, forming itself a part of the circuit. The reaction mass is an excellent conductor of the electric current at a high temperature. The barium oxide thus obtained is of a high degree of technical purity and possesses a uniformly porous structure.

The electrolytic process has been developed in the wet way by the Siemens & Halske Co., of Berlin (German Patent No. 241,043, of 1910). They make use of the facts that chloric acid and perchloric acid are only slightly affected by either the nascent oxygen liberated on an anode or the nascent hydrogen freed on a cathode, especially in the latter case, if the cathode is of silver or platinum. Use is made of a diaphragm apparatus. Solutions of barium chlorate or perchlorate serve as electrolytes. Barium carbonate is suspended in the anode cell, so that the acid liberated is immediately neutralized while the equivalent amount of barium oxide is formed in the cathode cell.

M. Herzberg proposes in his patent of 1907 (German Patent No. 195,278) to facilitate the decomposition of barium carbonate at a white heat by introducing substances that react with carbonic oxide and thus remove it. He accomplishes this, for example, by mixing barium peroxide with the carbonate.

Siemens & Co. (German Patents No. 158,950, of 1903, and No. 200,987, of 1907) claim to secure very good results by heating a mixture of barium carbonate, barium nitrate, and coal in an electric furnace to a white heat. The reaction is:

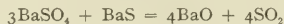


The decomposition of the carbonate begins as soon as nitrous vapors are evolved. Explosions are avoided by mixing the components with tar, and forming the mass into sticks. The process is continuous, and the resultant product is quite porous.

A somewhat similar method has been introduced by H. Schulze to change compact masses of barium oxide into the porous form. The oxide is mixed with barium nitrate and powdered coal, and this mixture is heated in an ordinary retort kiln or in an electric furnace. Favorable proportions are 88.5 parts of barium oxide, 10 parts of barium nitrate, and 1.5 parts of coal dust. The reaction is violent, and the product quite porous, in consequence of the large volume of gas liberated.

REDUCTION OF BARIUM SULFATE WITH COAL IN ELECTRIC FURNACE

Bradley and Jacobs (German Patent No. 111,667, of 1898) claim to secure fair results by the reduction of barium sulfate, with coal in an electric furnace. The basis of the reaction is the interaction between resultant barium sulfide and unchanged sulfate:



In practice the operation yields a mixture of 60 per cent BaO and 40 per cent BaS. After extraction with hot water, barium hydrate crystallizes from the solution. The same chemists claim to secure BaO in an exceedingly porous form by fusing together, at an elevated temperature, a mixture of barium carbide and barium hydrate in molecular proportions. The residue, after the expulsion of all hydrocarbons, consists of highly porous barium oxide (German Patent No. 142,051, of 1898).

ELECTROLYSIS OF AQUEOUS SOLUTIONS OF BARIUM SULFIDE

Brochet and Ranson (German Patent No. 129,324, of 1901) secure the hydrate by submitting aqueous solutions of barium sulfide to electrolysis. The concentration is 90 grams of sulfide in the liter for the solution in contact with the iron anode. A diaphragm is used, and the temperature is maintained at 50° C. The current employed has a tension of 1½ volts and a force of 5 amperes per square decimeter. A dilute solution, containing 50 grams per liter, is introduced in the cathode compartment.

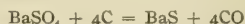
Barium hydrate is formed in this compartment and remains in solution while the temperature is maintained at 50°. From time to time the solution is drawn off, and the hydrate crystallizes out on cooling. Conductivity is increased by adding chlorides to the solutions. The addition of a layer of paraffin oil prevents any formation of carbonate. If chlorides are present, porous chloride is formed about the anode. This reacts with the sulfides in solution, and a precipitate of sulfur and of ferrous sulfide is gradually deposited.

H. Nordlinger (German Patents No. 132,433 and No. 133,691, of 1901) has devised a method for decolorizing the solutions of barium sulfide obtained by the lixiviation of the crude product resulting from the reduction of heavy spar with coal. He adds 1 per cent to 2 per cent of a solution of caustic soda (36° Baumé). All color vanishes and there is a marked increase in the readiness to crystallize, the crystals being perfectly colorless. Similar effects are produced by the addition of ammonia water. The introduction of a slight amount of formaldehyde overcomes all danger of oxidation.

W. Mostowitsch has lately investigated the reduction of barium sulfate by heating with coal. He finds that the reaction begins at 600° C. and is completed at 800° C. At lower temperatures the reaction is:



At higher temperatures it is:



Barium sulfide remains unchanged at a temperature of 1,000° C.

In producing barium hydrate from crude solutions of barium sulfide, G. Schreiber (German Patent No. 154,498, of 1902) recommends the following method: The liquid is saturated with hydrogen sulfide, and the resultant solution of barium sulfhydrate is concentrated in a vacuum apparatus. This is treated with cold, concentrated solutions of the alkaline nitrates or of calcium nitrate (Norway saltpeter), and barium nitrate is precipitated. The crystalline product is purified in a centrifugal.

An important advance in this field has been achieved by K. Puls, K. Krug, and coworkers (German Patent No. 198,861, of 1907), who also make use of the cheap and relatively pure calcium nitrate now supplied in increasing quantities by the Norwegian works. Witherite, BaCO₃, is finely ground and introduced into an aqueous solution of the nitrate. The mixture is then heated in a digester, provided with an agitator, under a pressure of from 1 to 2 atmospheres for 4 hours. After removal from the digester, water is added and the mass boiled. The precipitate of calcium carbonate is removed by means of a filter press and the residual solution of barium nitrate evaporated to the point of crystallization.

Trainé and Hellmers (German Patent No. 204,476, of 1907) propose a variation to this method. Instead of witherite they employ barium oxalate or barium phosphate, which has been precipitated from solutions of barium sulfide.

An important process for the reduction of barium sulfate that promises to simplify materially the manufacture of soluble barium compounds is due to C. A. Béringer, of Charlottenburg (German Patent No. 249,857, of 1912). He keeps a mixture of heavy spar (7 parts) and clay (3 parts) for some time at a bright red heat and brings about the formation of a double silicate of barium and aluminum. This is readily susceptible to decomposition by hydrochloric or nitric acid.

PEAT AS FUEL¹

Reports of the growing use of peat as fuel in Europe have stimulated the interest of owners of peat land in the United States, especially in those parts of the country where other fuels are high in price, and many attempts have been made to make

¹ Abstract of paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1912.

peat fuel on a commercial scale in this country, so far without success.

A careful analysis of the reasons for this failure, however, shows that not the peat, but easily remedied causes, largely due to ignorance and inexperience, were responsible for the failures. Such peat fuel as has been produced has always been sold readily at satisfactory prices. It, therefore, seems worth while to examine into the possibilities of peat as fuel and learn if it may not have a place as an auxiliary fuel, at least, in the parts of the country where it is found to relieve those consumers who are remote from coal mines from the high prices which other fuels now command.

Upwards of 15,000,000 tons of peat fuel are produced and used annually in Europe, and its use for the production of steam and electric power is noticeably increasing in countries where peat is abundant, although as heretofore the great part of the peat fuel is used for domestic consumption.

In the United States peat is found in abundance in the region north of the Ohio River and east of the 100th Meridian. It also occurs in New York and New England and along the Atlantic Coastal plain to Florida which has large peat deposits and on the Pacific Coast in California, Oregon, and Washington. It will be seen that this distribution is such that the peat deposits are almost entirely in States with little or no coal.

The chief characteristic of peat which makes its production for fuel difficult is that it always contains a high water content (from 85 to 90 per cent) which must be removed before the peat can be burned. All processes for preparing peat fuel are based on attempts to remove the water cheaply and certainly. They are made difficult by the fibrous and woody material of which the peat is composed and by the peculiar water-holding power of the organic chemical compounds present. The water mixed with the peat cannot be removed from masses of the solid materials either by pressure or by centrifugal force below about 70 per cent.

Commercial methods of producing peat fuel are limited at the present time to those which depend, in large part, at least, on drying the peat by exposure to the air. A few cases are reported where the peat is partly air-dried and the moisture farther reduced by the use of artificial heat. The greater part of the peat fuel made and used in Europe is in the form of air-dried bricks or blocks which have been either cut from the bog with special spade-like tools, or formed by machines which first grind or macerate the wet peat to a pulp and then shape it into bricks. Some processes spread the pulp on the surface of a drying ground in a thin sheet and form the bricks by marking the sheet with properly spaced markers. When partly dried, the peat is turned by hand labor, then piled in small heaps for a time, and finally stacked till used: the product is called machine peat. Recently devised machines seem likely to eliminate most of the hand labor from the methods now in use abroad for making machine peat, and thus do away with one important objection to its use in the United States. Air-dried machine peat is the kind of peat fuel used in power and industrial works in Europe, with very few exceptions.

Briquetting peat has been tried in many countries and the most notable failures at peat fuel production in the United States have been of plants of this kind. At present peat briquets are made in but very few places in Europe, and the quantity produced is small. A much larger and more costly plant is needed to make briquets than is required for air-dried machine peat, and more money is required to run it.

PEAT CHARCOAL OR COKE

Machine peat may be coked in proper retorts and wood alcohol, acetic acid, ammonia and tar and tar derivatives may be recovered as by-products. The charcoal thus obtained is equal to first-rate wood charcoal for metallurgical work. In

Europe, there are well established peat coke plants, which have been running a number of years.

The most promising use of peat is in gas producers for generating power or fuel gas. Plants equipped with properly designed gas producers, with or without apparatus for the recovery of by-products and located near the bogs from which the fuel is taken, are being successfully operated in a number of European countries to generate electricity for lighting and power purposes in nearby towns. Some of these plants use peat with as high as 60 per cent moisture and are reported to recover enough ammonia as sulfate to pay the cost of getting the fuel and running the plant.

The fuel value of perfectly dry peat ranges from about 7,000 to above 11,000 B. t. u. This is reduced by the presence of moisture and high ash content.

It would seem that our peat resources are well worth developing whenever additional fuel supplies are needed for the development of the country.

CHARLES A. DAVIS

BUREAU OF MINES
WASHINGTON, D. C.

LIFE OF PLATINUM CRUCIBLES LENGTHENED BY SUBSTITUTION OF MEKER BURNER FOR BLAST LAMP IN CARBON DETERMINATIONS

For some time several platinum crucibles were in use in this laboratory for the determination of carbon by direct combustion. Blast lamps were used as the source of heat, the usual precautions being observed for flame regulation. The crucibles were used continuously until the bottoms began to crack or became appreciably pervious to gas. They were repaired in every case by the same Company, the weight of the newly repaired crucibles and the thickness of the bottoms being uniform. The average working life under these conditions covered five hundred to six hundred combustions per crucible, the maximum being about nine hundred.

Meker burners were substituted with entire success for the blast lamps. After five thousand combustions had been made in each crucible, one became slightly pervious to gas. The use of this crucible was discontinued shortly afterwards, the others being in good condition.

R. J. WYSOR, *Chief Chemist*

BETHLEHEM STEEL CO.
SOUTH BETHLEHEM, PA.

SYNTHETIC TANNIN

Consul Benjamin F. Chase, Leeds, England advises that what is said to be a successful synthetic tannin has been discovered by Dr. Edmund Stiasny, assistant professor of the leather industries laboratories of the University of Leeds. The new tannin, which is called Neradol, is made from tar distillation products, the synthesis being carried out by sulfonating cresylic acid and combining it then with formaldehyde. The white color of the Neradol-tanned leather and the brightening and bleaching effect of Neradol when used in combination with other tannins (vegetable and chrome) are especially noteworthy. The Leather Trades' Review states:

Neradol is somewhat similar to ordinary tanning extract, and forms a light brown solution in cold water. It is a pure tannin of 30 per cent strength according to the hide powder method, and can be used in smaller quantities to obtain the same effects as those at present produced by the ordinary agents.

Dr. Stiasny has made a series of tests on hides and sheep and calf skins and has recently showed samples of leather ranging from light glazed kid to sole leather produced either with synthetic tannin alone, or with it in combination with vegetable tannin, chrome, or wood-pulp liquors. In every case the product appeared to be satisfactory, the leather being supple, fine, and

strong in the case of the light skins, while the sample of insoling belly was flexible and clear and light in color. However, the synthetic product is not likely to greatly interest the sole-leather manufacturer while it is the custom to sell such leather by weight, as the new tannin does not give weight; in fact, it produces a light tannage, and is, therefore, more likely to find commercial application in the manufacture of light leathers. But it is said to be useful in the early stages of sole-leather tanning to prevent drawn grain.

FUTURE USES OF THE NEW TANNIN

It is quite possible, especially when it can be produced more cheaply—the price is stated to be about \$97 per long ton—that the adoption of Neradol tannage may have to be seriously considered by those interested in chrome tanning. Meanwhile it is probable that this synthetic material may be used in conjunction with both vegetable and chrome tannages, as it is claimed that it considerably hastens the process, and that, contrary to the general effect of quick processes, it improves the quality of the leather at the same time. It is stated that it has been already used on a fairly large scale in the German tanning industry. An advantage of the new tannin is that it can be prepared in a uniform manner, and the material is not subject to chemical changes.

An interesting experiment recently carried out consisted in placing a piece of calf pelt, which was badly discolored, in a solution of the synthetic tannin. After a few minutes the discoloration had completely disappeared, and the pelt was almost white. In about two hours the pelt was struck through with the tannin. The time occupied in tanning the various samples shown by Dr. Stiasny varied from two days to a few weeks. The combination tannage of Neradol, wood pulp, and vegetable tannin on a stout sheepskin took four days.

IMPORTS OF OLIVE OIL NOT ADULTERATED

Following the receipt of several inquiries as to whether a large part of the olive oil imported into the United States is adulterated with cotton-seed oil, the Department of Agriculture has made a special investigation into the state of the olive oil admitted. The government's interest in the matter is two-fold: *first*, to protect the people from getting adulterated olive oil; *second*, to protect the reputation of olive oil in the interest of olive oil producers in California, Arizona, and other olive-growing sections. Since 1900, the Department, through its various port laboratories, has examined samples from 2149 importations of olive oil. Of these, only ten were refused entry, and only three of these were refused entry for containing cotton-seed oil. These cotton-seed oil adulterations date back to 1908, when two shipments were found to be adulterated, and 1909, when one shipment was found to be adulterated. Since that time, there has been no shipment which has given evidence of cotton-seed oil adulteration. In 1910, seven shipments of olive oil were refused admission because adulterated with peanut oil, and since that time there have been no cases discovered of either cotton-seed oil or peanut oil adulteration. The addition of cotton-seed oil to olive oil, the government specialists report, is very easily detected. Indications therefore are that all olive oil admitted to the country and branded as olive oil has been pure olive oil, and has contained no cotton-seed or peanut oil. Occasionally the government discovers shipments of sardines in which the olive oil contains some cotton-seed oil. The experts point out that it would be illogical for the importer to bring into this country olive oil adulterated with cotton-seed oil, and pay a duty of 50 cents a gallon on the cotton-seed oil that is contained in the mixture. Similarly, nut oils are admitted under the tariff act, and the specialists say that it would be absurd for an importer to bring from Holland olive oil adulterated with peanut oil, and pay a duty of 50 cents a gallon on the mixture, when he could bring

them over separately and avoid paying any duty on the nut oil.

U. S. DEPT. OF AGRICULTURE,
OFFICE OF INFORMATION

CRISIS IN GERMAN POTASH INDUSTRY

Consul Talbot J. Albert, Brunswick, says that all the German commercial newspapers of May 23, 1913, report a serious financial crisis in the potash industry. The funded securities of the leading mining companies of the Potash Syndicate, which had been regarded as gilt-edged and were selling at high premiums, have fallen below par. The obligations and stocks of other mining companies have fallen, some of them to more than one-half of their former quoted value. A number of newly established companies have become insolvent. The cause of this alarming condition of the industry is overproduction.

The potash law passed two years ago primarily for putting an end to the concessions granted by certain mining companies to American importers accomplished that object, but has failed to limit the production of potash. The allowance under the law of *sales quotas* to new mining companies entering on the stage of production led to a rush on the part of old companies to sink new shafts in order to maintain their *quotas* and to the establishment of a great many new mining companies. The consequence has been overproduction and a general collapse of the industry. It will probably take several years to equalize the supply with the demand for potash. Legislation is now pending to amend the potash law so as to regulate the production, but so far it has been found impracticable to frame the necessary regulations.

POWER FROM WASTE HEAT

Consul Walter C. Hamm, Newcastle, England, states that West Hartlepool, which can claim to be the first municipal authority to produce electricity by means of waste heat, will open its new generating station in the course of two or three weeks. The two turbo-generators, each of 1,500 kilowatts, will be driven by exhaust steam from the furnace-blowing engines of the Seaton Carew Iron Co., adjacent to whose works the station is built. In return for their exhaust steam, which has hitherto been blowing to waste in the air, the Seaton Carew Iron Co. will receive free from the corporation the supply of electric current they need at their works.

Expenditure on coal will practically be eliminated. The coal bill for the present electricity station is about \$20,000 a year, and, as it is anticipated that the consumption of current will largely increase under the cheaper rate now possible, the ultimate saving by the use of waste heat will be very considerable. Should the supply of exhaust steam not be available, either through a breakdown of the blowing engines or through the iron works being idle, a supply of high-pressure steam will be obtainable from the Seaton Carew Iron Co.

The total expenditure involved in connection with the new scheme is \$188,500, the plant alone having cost \$150,000. The old generating station will be maintained as a stand-by, and also as a town sub-station. There the current from the new station will be transformed to the voltage required for distribution to the town.

GERMAN RECORD PRODUCTION OF RAW IRON

Vice-Consul General DeWitt C. Poole, Jr., Berlin, writes that the production of raw iron in Germany during May, 1913, surpassed all previous records. The total output amounted to 1,641,600 metric tons, as compared with 1,587,300 in April, 1913, and 1,492,157 in May, 1912. The various sorts produced during May were: Foundry pig, 309,892 tons; Bessemer, 29,406; Thomas, 1,049,524; steel and spiegel, 207,227; and puddle, 45,551.

BOOK REVIEWS

A Manual of Cement Testing. By WILLIAM ALLYN RICHARDS AND HENRY BRIGGS NORTH. x + 137 pp., illustrated. New York: D. Van Nostrand Co. 1912. Price, \$1.50.

This little manual is designed for the use of engineers and chemists in colleges and in the field. The authors state that it is intended to assist in bringing about uniformity in the testing of cement, and while its aid along this line would be greater if it went more into detail with reference to the little points of manipulation which influence so largely this one thing, still the book will no doubt prove of value as a text-book, when supplemented by competent instruction to supply this deficiency. In the main, only the methods of test recommended by the American Society of Civil Engineers are given, and, while the student should be taught these, the reviewer can but regret the omission of all reference to the use of Gilmore needles for determining the setting time. In fully 99 per cent of the cement tests which are made this apparatus is employed. In several instances, the standard rules have been replaced by methods which have neither the fact of extensive usage nor ease of manipulation to recommend them—notably the substitution of a purely empirical formula for the standard table giving the percentage of water with sand mixtures—while the rules laid down for the acceptance and rejection of a cement as given on page 38 hardly agree with the interpretation ordinarily placed upon the specifications by most inspectors and engineers.

Under the heading of chemical analysis, the authors have substituted a method of their own for the analysis of limestone which is decidedly inaccurate, in that simple solution in hydrochloric acid is undertaken without the previous ignition prescribed by the standard method. If the authors wished to deviate from the latter, descriptions of the bichromate method for iron and the volumetric (permanganate) method for lime, which are so extensively used in the analysis of cement, might have been included to advantage.

RICHARD K. MEADE

Coal, and the Prevention of Explosions and Fires in Mines.

By JOHN HARGER. 183 pp. Andrew Reid & Company, Limited London. Longmans, Green & Co., New York. Price, \$1.25.

As stated in the Preface, the information contained in this book has been collected from Government blue-books and various journals, while some of it is the result of the author's original work at coal pits and in the chemical laboratories of Liverpool University.

The scope of the work covers the origin of coal and its composition, with particular reference to the nature of its constituents in their original form. The subject of occluded gases has been reviewed, together with both slow and rapid oxidation, oxygen requirements for same, and effect of inert gases. Two chapters are devoted to respiration, giving general functions of oxygen and carbon dioxide, and also the influence of water vapor at different temperatures, carbon dioxide, and other gases.

The subject of explosions, with particular reference to that of coal dust, is then taken up and a brief review made of the explosions which have occurred up to the present time, together with a very brief summary of reports, with particular reference to those occurring in Great Britain. The writer then takes up the phenomena of dust explosions and makes comments upon the methods used at Altfot's Station, and also mentions the work of the United States Bureau of Mines, French Government, and others.

In general, the author is quite severe in his criticism, relative to the conclusions reached concerning explosions and methods carried out by the different governments in the study of same. His conclusions seem to be that hitherto, research work on coal mine explosions has been conducted mainly by amateurs and by government commissions, and what is wanted is the method

of preventing explosions, not of making them. Some statements he has made relative to cause of explosions, which have occurred in this country, show lack of familiarity with the facts of the case. He also makes the statement that the high death rate in the mines of the United States is due chiefly to the abundance of gas and dust explosions, thus showing an unfamiliarity with facts, for during nine years, gas and dust explosions have caused less than 17 per cent of the deaths that have occurred in the bituminous mines of the United States.

The principal object of the book seems to be to advance ideas which the author has relative to minimizing the possibility of dust explosions by reversing the direction of ventilation at least once a week, so that by this reversal the ventilating currents will dislodge the fine dust which accumulates on ledges, crevices, etc.; also by preventing both gas and dust explosions, as well as gob fires, by introducing a considerable percentage of CO₂ into the ventilating air so as to maintain a percentage of oxygen of 17 per cent or less, so as to make combustion of such to be an impossibility on account of the deficient amount of oxygen. This would necessitate the use of electric or acetylene lights, and the author claims that no detrimental effect would be felt by the miners in their work.

To a great extent, the remedies and conclusions which the author has given, are more applicable to the deep and hotter mines obtaining in England and European countries, where there is ample initial heat to start spontaneous combustion, and also where the carrying of high humidity in the air for ventilation would make very oppressive conditions for the miner on account of the high temperature.

On the whole, the book is an interesting contribution to the very important subject that is now receiving a great deal of consideration in this country.

E. G. BAILEY

"New and Non-official Remedies, 1911." American Medical Association Press, 535 Dearborn Avenue, Chicago. pp. 282.

This book contains descriptions of the medicinal substances which, prior to January 1, 1911, have been examined by the Council on Pharmacy and Chemistry of the American Medical Association, which appeared to comply with the rules of the Council, and which, therefore, were accepted for insertion in the annual "New and Non-official Remedies." The descriptions are comprehensive, yet concise, and, if one appreciates the object of the Council, no criticism can be advanced against either method or purpose. The indexing is especially well done. The book should be in the hands of all interested in pharmaceutical chemistry.

W. A. HAMOR

The Natural History of Clay. By ALFRED B. SEARLE. University Press, Cambridge, 1912. 176 pp. 18 illustrations.

This little volume endeavors to present a brief treatment of the properties of clays, their origin, the modes of their accumulation and the character and structure of the clay substance. The discussion of the physical character of clays is interesting and suggestive, though a somewhat more detailed and quantitative account would have been desirable. The treatment of geological occurrence of clays refers to the geology of England. From a general standpoint the subjects of the origin and accumulation of clays are well handled, as is the topic "commercial clays." No attempt is made to give specific information. The discussion of the theoretical and actual clay substance is interestingly written. The little book should be of value to those who desire a general knowledge of clays, but is not intended for technical students desiring detailed information.

A. V. BLEININGER

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York

- Alcohol.** LOUIS JACQUET. 8vo., pp. 945. Price, \$3.50. Paris, 1913. (French.)
- Alkaloids, The Plant.** THOMAS A. HENRY. 8vo. Price, \$4.50. J. & A. Churchill, London.
- American Institute of Chemical Engineers, Transactions V.** 8vo., pp. 284. D. Van Nostrand & Co., New York.
- Ammonia Vapor, The Properties of Saturated and Superheated.** G. A. GOODENOUGH AND WM. EARL MOSHER. 8vo., pp. 94. Price, \$0.50. University of Illinois Engineering Experiment Station Bulletin, No. 66.
- Asphalts and Bitumens, Natural Rock.** ARTHUR DANBY. 8vo., pp. 244. Price, \$2.25. Constable & Co., London.
- Cements, Action of the Salts in Alkali Water and Sea Water on.** P. H. BATES, A. J. PHILLIPS AND RUDOLPH J. WIG. L. 8vo., pp. 157. U. S. Bureau of Standards. Technologic Paper No. 13.
- Chemical Engineering, Handbook of.** G. E. DAVIS. 2 Vols. 8vo. Price, \$10.50. Davis Bros., London.
- Chemistry, First Principles of.** BROWNLEE, FULLER, HANCOCK, SCHON AND WHITSIT. 8vo., pp. 421. Price, \$1.25. Allyn & Bacon, Boston.
- Chemistry, Text-book of.** E. HEINZ AND R. WAEBER. 3d edition. 8vo., pp. 192. Price, \$0.75. F. Hirt & Son, Leipzig. (German.)
- Disinfectants, Coal-Tar.** WORTH HALE. 8vo., pp. 41. Price, \$0.05. U. S. Public Health Service, Hygiene Laboratory Bulletin 88.
- Essential Oils and Artificial Perfumery, The Chemistry of.** ERNEST J. PARRY. 2d edition. 8vo. Price, \$3.50. Oil & Color Trades Journal, London.
- Essential Oils: Scientific and Industrial Bulletin of Roure-Bertrand Fils. Series III, No. 7, Apl. '13.** 8v. 8vo., pp. 147. Roure-Bertrand Fils, Grasse.
- Fats, Lipoids and Waxes, Chemistry of the.** W. GLIKIN. 2 Vols. 8vo., pp. 1500. Price, \$10.50. Gebrueder Borntraeger, Berlin.
- Fertilizers, Chemical, Production and Consumption of, in the World.** ANONYMOUS. 8vo., pp. 134. Price, \$0.75. Institut International d'Agriculture, Rome. (French.)
- Inorganic Chemistry, The Methods of, Vol. I.** A. STAEBLER. 8vo., pp. 787. Price, \$6.25. Veit & Co., Leipzig. (German.)
- Iron and Steel Industry, Electric Furnaces in the.** RODENHAUSER & SCHOENAWA. 8vo. Price, \$4.00. Chapman & Hall, London.
- Nitro-derivatives, Manufacture of the.** E. GRANDMOUGIN. 8vo. School of Chemistry, Mulhouse.
- Oils and Fats, Carbohydrate, Examination of.** D. HOLDE. 4th edition. 8vo., pp. 612. Price, \$4.50. Julius Springer, Berlin. (German.)
- Organic Chemistry, Literature Index of.** R. STELZNER. Lex. 8vo., pp. 1280. Price, \$16.00. Deutsche Chemische Gesellschaft, Berlin. (German.)
- Organic Chemistry, Richter's. Vol. II.** R. ANSCHUTZ AND H. MERWEIN. 2 Vols. 11th edition. 8vo. Price, \$6.50. Friedrich Cohen, Bonn. (German.)
- Paints: A Manual of Painters' Colors, Oils and Varnishes.** G. H. HURST. 5th edition. Cr. 8vo., pp. 540. Price, \$4.00. C. Griffin & Co., London.
- Potash Industry, The Effluents of the.** DUNBAR. 8vo. Price, \$2.00. R. Oldenburg, Munich. (German.)
- Sugar Juices, Evaporation of.** HORSIN-DEON. 8vo., pp. 200. Price, \$1.00. L. Geisler, Paris.
- Sugar Manufacture.** SIEGMUND FEITLER. 8vo. Price, \$1.25. Alfred Hoelder, Vienna. (German.)
- Sugar, The Manufacture of.** D. SIDERSKY. 8vo., pp. 356. Price, \$1.00. O. Doin et Fils, Paris.
- Steel, Liquid.** DAVID CARNegie. 8vo., pp. 520. Price, \$7.50. Longmans, Green & Co., New York.
- Textile Industry, Handbook of the.** O. ROTH, F. BRENGER, K. FIEDLER, et al. 9 Vols. 8vo. Price, \$9.00. M. Jaenecke, Leipzig. (German.)
- Wood-Waste, The Utilization of.** ERNEST HUBBARD. 2d edition. Cr. 8vo., pp. 192. Price, \$1.50. Scott, Greenwood & Co., London.
- Cement, Artificial Portland, The Properties of.** By ROBERT ADAM. *Revue générale de Chimie pure et appliquée*, Vol. 16, 1913, No. 9, pp. 161-165.
- Cement, the Autoclave Test for.** By H. J. FORCE, A. S. CUSHMAN, et al. *Engineering Record*, Vol. 68, 1913, No. 1, pp. 13-19.
- Coke-Oven Carbonization.** By W. CHANEY. *Journal of Gas Lighting*, Vol. 122, 1913, No. 2615, pp. 938-947.
- Corrosion; A New Chemical Cause of the Rusting of Iron.** By WILHELM VAUBEL. *Chemiker Zeitung*, Vol. 37, 1913, No. 69, pp. 693-694.
- Corrosion, Electrolytic, of Iron in Soils.** By B. MCCOLLUM AND K. H. LOGAN. *Proceedings American Institute of Electrical Engineers*, Vol. 32, 1913, No. 7, pp. 1515-1575.
- Drying, Problems in Vacuum.** By J. P. DEVINE. *India Rubber World*, Vol. 48, 1913, No. 4, pp. 508-510.
- Explosives, Modern and Their Use.** By F. H. GUNSOLUS. *Journal of the Cleveland Engineering Society*, Vol. 5, 1913, No. 6, pp. 407-415.
- Fertilizers, Sampling of.** By J. S. BROGDON. *American Fertilizer Handbook*, Vol. 1, 1913, No. 1, pp. 76n-76p.
- Food Chemistry in 1912. A Review.** By J. RUEHL. *Zeitschrift fuer angewandte Chemie Aufsatzteil*, Vol. 26, 1913, No. 45, pp. 331-343.
- Fuels, Water Formation during the Dry Distillation of.** By RAU AND LAMBRIS. *Journal fuer Gasbeleuchtung*, Vol. 56, 1913, No. 23, pp. 533-537.
- Gas, Coal, Liquid Purification of.** By W. B. DAVIDSON. *Journal of Gas Lighting*, Vol. 122, 1913, No. 2615, pp. 948-958.
- Gas, Illuminating, and Coke in 1912. A Review.** By ARTHUR FUERTH. *Zeitschrift fuer angewandte Chemie Aufsatzteil*, Vol. 26, 1913, No. 45, pp. 343-351.
- Gases, Blast Furnace, The Purification of.** By C. HERWEGH. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 7, pp. 399-403.
- Heating, Gaseous.** By E. W. SMITH AND C. M. WALTER. *Journal of Gas Lighting*, Vol. 122, 1913, No. 2615, pp. 958-969.
- Iron and Steel, Oxygen in, Value of Existing Methods for Its Determination.** By WM. R. FLEMING. Reprint, *Proceedings American Society for Testing Materials*, Vol. 16, 1913, 10 pp.
- Microscopic Determination of Minerals.** By ALFRED J. MOSES. *School of Mines Quarterly*, Vol. 34, 1913, No. 4, pp. 305-334.
- Paints and Varnishes, Rational and Irrational Methods of Accelerating the Drying of.** By J. G. MCINTOSH. *Oil and Color Trades Journal*, Vol. 43, 1913, No. 763, pp. 1931-1936.
- Paints; Report of Committee D-1 on Preservative Coatings for Structural Materials.** Reprint, *Proceedings American Society for Testing Materials*, Vol. 16, 1913, 96 pp.
- Pernanganate Solution, Potassium, Standardization of, by Sodium Oxalate.** By R. S. MCBRIDE. *Bulletin U. S. Bureau of Standards*, Vol. 9, 1913, No. 1, pp. 611-642.
- Petroleum; Liquid Fuel.** By VIVIAN B. LEWES. *Journal Royal Society of Arts*, Vol. 61, 1913, No. 3158-9, pp. 690-695 and 702-707.
- Petroleum Products, The Manufacture of.** By F. C. ROBINSON. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 7, pp. 389-394.
- Pigments, the Manufacture of, as Seen by the Insurance Engineer.** By JOEL R. WILSON. *The Armour Engineer*, Vol. 5, 1913, No. 2, pp. 147-156.
- Power Transmission by Cotton Ropes.** By E. EDWARD HART. *Pulp and Paper Magazine of Canada*, Vol. 11, 1913, No. 12, pp. 419-426.
- Radio-active Elements.** By C. H. VIOL. *Radium*, Vol. 1, 1913, No. 3, pp. 8-12.
- Rubber Industry, Some Problems of the.** By H. E. POTTS. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 11, pp. 564-568.
- Rubber, The Preparation of Plantation Para.** By B. J. EATON. *India Rubber Journal*, Vol. 45, 1913, Nos. 21 and 22, pp. 21-23 and 14-16.
- Sewage, Permissible Dilution of.** By GEORGE W. FULLER. *Journal of the Western Societies of Engineers*, Vol. 18, 1913, No. 5, pp. 382-397.
- Steel, Production of Sound, by Lateral Compression of the Ingot while Center is Liquid.** By BENJAMIN TALBOT. *Industrial World*, Vol. 47, 1913, No. 23, pp. 678-683.
- Sugar Industry for 1911 and 1912. Review of the.** By RENÉ VALLIER. *Revue générale de Chimie pure et appliquée*, Vol. 16, 1913, No. 9, pp. 149-161.
- Sugar Manufacture, The By-Products of, and Methods for Their Utilization.** By C. A. BROWNE. *School of Mines Quarterly*, Vol. 34, 1913, No. 4, pp. 370-382.
- Sugar, Some Experiments in Clarification in Louisiana.** By WILLIAM E. CROSS. *American Sugar Industry*, Vol. 15, 1913, No. 6, pp. 25-30.

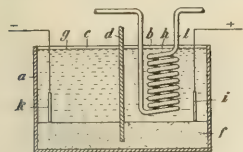
RECENT JOURNAL ARTICLES

- Artificial Silk from Cotton, The Manufacture of.** By H. R. CARTER. *Cotton*, Vol. 79, 1913, No. 8, pp. 319-320.
- Bakelite and Its Applications.** By H. LEBACH. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 11, pp. 559-564.
- Brass; The Analysis of Copper-Tin Alloys.** W. GEMMELL. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 11, pp. 581-585.
- Fuels, the Heat Value of, Calorimetric Determination of.** By HERMANN THIELE. *Zeitschrift fuer angewandte Chemie Aufsatzteil*, Vol. 26, 1913, No. 49, pp. 370-375.
- Caoutchouc, The Structure and Molecular Weight of.** By FRANK E. BARROWS. *The Armour Engineer*, Vol. 5, 1913, No. 2, pp. 167-178.

RECENT INVENTIONS

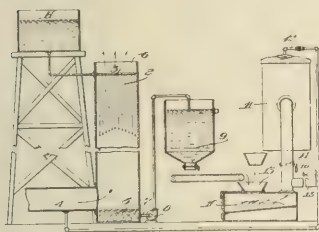
By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Precipitating Ulmic Compounds from the Black Liquors of Soda Pulp-Mills. N. A. Langlet, May 20, 1913. U. S. Pat. 1,062,016. Sodium chlorid is added to the liquor after which



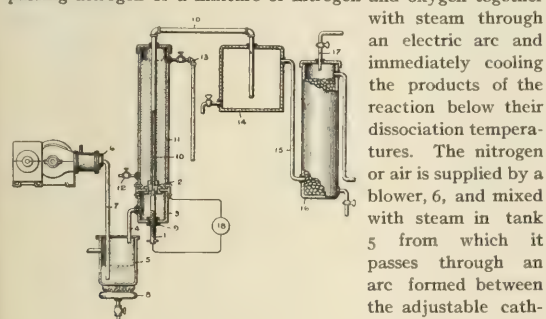
it is subjected to electrolysis at an elevated temperature. The electrolytic vessel employed has anode and cathode chambers divided by a porous diaphragm. The liquor to be treated is placed in the anode chamber and a solution of sodium sulfate, carbonate or hydroxid in the cathode chamber.

Obtaining Sulfur from Smelter Gases. Sanborn, McMahon, Overbury and Young, May 20, 1913. U. S. Pat. 1,062,120. Sulfurous fumes from the flue 4 are subjected to a spray of calcium sulfide solution to absorb the sulfur dioxide. The resulting sludge is pumped to a settling tank. Subsequently the solids from the settling tank are transferred to a regenerating furnace, 10, where, after being dried at a low heat, they are subjected to a sufficient



temperature to distill off the sulfur which collects in the condenser chamber 11. The residue from the sulfur distillation in the furnace is mixed with coke and the temperature raised to reduce the residue to calcium sulfide which is returned to the tank A for re-use.

Ammonium Compounds. C. Steinmetz, May 27, 1913. U. S. Pat. 1,062,805. Nitrate and nitrite of ammonia are formed by passing nitrogen or a mixture of nitrogen and oxygen together with steam through an electric arc and immediately cooling the products of the reaction below their dissociation temperatures. The nitrogen or air is supplied by a blower, 6, and mixed with steam in tank 5 from which it passes through an arc formed between the adjustable cathode 1 and the perforated anode 2. The products of the reaction are immediately cooled by contact with the cooled walls of the tube 10.



The unacted upon water vapor is condensed in the chamber 14 and forms a strong solution of ammonium nitrate and nitrite. The uncombined nitric and nitrous acids or ammonia pass over into the absorption tank 16 where they are dissolved.

Tinning and Leading Metals. F. Plathner and V. Dorn, May 6, 1913. U. S. Pat. 1,060,938. The coating metal in the form of a fine powder is mixed with a suitable flux and a liquid vehicle completely volatile at a temperature below the melting point of the coating metal. The mixture is spread on the surface to be coated and the whole heated until the vehicle is

volatilized and the powdered metal melted and fluxed to a thin adherent coating.

Producing Fine Tungstous Oxids. K. Farkas, May 6, 1913. U. S. Pat. 1,061,058. The yellow tungstic anhydrid is heated to a high temperature in a constantly renewed atmosphere of carbon dioxide.

Baking Powder. W. Klapproth, May 6, 1913. U. S. Pat. 1,061,183. The composition comprises normal lactate of aluminum and an alkaline carbonate.

Regenerating Iron Oxid in Gas Purification. D. McDonald, May 13, 1913. U. S. Pat. 1,061,859. The spent iron oxid is fired under a hood connected with a stack, air being admitted through the openings c. The oxid is fired by means of its impurities as fuel which burns on the surface, and as the spent material is reduced to ferric oxid it feeds down the pile by reason of its finely divided condition, and is collected at the base.



Production of a Plastic or Elastic Substance. Julius Stockhausen, May 13, 1913. U. S. Pat. 1,061,881. The process consists in mixing gelatin with glycerin and camphor in solution in acetone and treating the mass with sulfur.

Metallurgy of Iron and Steel. W. S. Simpson and H. Oviatt, May 13, 1913. U. S. Pat. 1,061,950. Metallic iron is produced from iron oxid ores by subjecting them and a suitable quantity of finely divided sodium chlorid and silica, to a high degree of heat.

Making Potash Alum. E. Hart, May 20, 1913. U. S. Pat. 1,062,278. Feldspar is heated with sodium sulfate and carbon and the resulting mass treated with sulfuric acid. Potash alum is obtained from the soluble portion of the product.

An Ammonium Superphosphate Fertilizer. T. L. Willson and M. M. Haff, May 27, 1913. U. S. Pat. 1,062,869. Ammonia gas is introduced into superphosphate and the product mixed with fresh superphosphate.

Producing Rubber-Like Compounds. H. S. A. Holt, May 27, 1913. U. S. Pat. 1,062,973. Isoprene is heated in the presence of about one-fifth of 1 per cent of sulfur.

Glue or Gelatin. G. Upton, June 3, 1913. U. S. Pat. 1,063,229. The glue stock is subjected to the action of steam in a digester and the glue formed together with water of condensation, removed from the digester, as separated.

Producing Low-Carbon Ferro-Alloys. J. M. Morehead, June 3, 1913. U. S. Pat. 1,063,280. A ferro-alloy high in carbon is formed, and this is subjected to the action of an oxidizing gas at a temperature at which the affinity of oxygen for the contained carbon is greater than its affinity for the alloyed metal.

Sulfid of Zinc. Koetschet and Meyer, June 3, 1913. U. S. Pat. 1,063,356. Crude zinc sulfate is subjected to a preliminary treatment with sulfuretted hydrogen to precipitate impurities. It is then filtered, concentrated and subjected to intimate and prolonged contact with sulfuretted hydrogen.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF JUNE, 1913

ORGANIC CHEMICALS

Acetanilid.....	Lb.	21	@	23
Acetic Acid (28 per cent).....	C.	2.00	@	2.15
Acetone (drums).....	Lb.	15 3/4	@	16
Alcohol, denatured (180 proof).....	Gal.	36	@	38
Alcohol, grain (188 proof).....	Gal.	2.46	@	2.48
Alcohol, wood (95 per cent).....	Gal.	47	@	49
Amyl Acetate.....	Gal.	2.20	@	2.30
Aniline Oil.....	Lb.	10 1/4	@	10 5/8
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	21	@	23
Camphor (refined in bulk).....	Lb.	42 1/2	@	44
Carbolic Acid (drums).....	Lb.	9 1/4	@	13
Carbon Bisulfide.....	Lb.	6 1/2	@	8
Carbon Tetrachloride (drums).....	Lb.	73 1/4	@	81 1/4
Chloroform.....	Lb.	25	@	35
Citric Acid (domestic), crystals.....	Lb.	44	@	45
Dextrine (corn).....	C.	2.80	@	3.40
Dextrine (imported potato).....	Lb.	6	@	7
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	18 1/4	@	18 1/2
Oxalic Acid.....	Lb.	7 1/8	@	8
Pyrogallie Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	29	@	31
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2.02	/	2.50
Starch (potato).....	Lb.	4 1/4	@	5
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	28 1/4	@	29 1/4
Starch (wheat).....	Lb.	5	@	6 1/2
Tannic Acid (commercial).....	Lb.	35	@	35
Tartaric Acid, crystals.....	Lb.	30 1/4	@	31

INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	73 1/4	@	8
Acetate of Lime (gray).....	C.	2.50	@	2.60
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate.....	C.	1.40	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	6 1/4	@	6 1/2
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	3 3/8	@	4
Barium Chloride.....	C.	1.70	@	1.80
Barium Nitrate.....	Lb.	5 1/4	@	5 1/2
Barytes (prime white, foreign).....	Ton	18.50	@	22.50
Bleaching Powder (35 per cent).....	C.	1.22 1/2	@	1.35
Blue Vitriol.....	Lb.	5 1/4	@	5 1/2
Borax, crystals (bags).....	Lb.	38 1/4	@	41 1/4
Boric Acid, crystals (powd.).....	Lb.	7	@	7 1/2
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	85	@	1.10
Chalk (light precipitated).....	Lb.	4	@	5
China Clay (imported).....	Ton	11.50	@	18.00
Feldspar.....	Ton	7.00	@	9.00
Fuller's Earth, powdered, Foreign.....	Ton	14.50	@	15.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.05	@	3.10
Lead Nitrate.....	Lb.	8 1/8	@	8 1/4
Litharge (American).....	Lb.	6 1/2	@	7
Lithium Carbonate.....	Lb.	65	@	70
Magnesia (powdered).....	Lb.	5 1/2	@	6
Magnesite (raw).....	Ton	30.00	@	31.00
Nitric Acid, 36°.....	Lb.	37 1/8	@	4 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	21 1/2	@	25 1/2
Phosphorus.....	Lb.	35	@	90
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 3/4	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined) 80 @ 85%.....	C.	3.40	@	3.65
Potassium Chlorate, crystals.....	Lb.	8 1/4	@	9 3/4
Potassium Cyanide (bulk) 98-99%.....	Lb.	19	@	24
Potassium Hydroxide.....	C.	3.00	@	4.75
Potassium Iodide (bulk).....	Lb.	2.60	@	2.65
Potassium Nitrate (crude).....	Lb.	5	@	—
Potassium Permanganate (bulk).....	Lb.	98 1/4	@	11
Quicksilver, Flask.....	40.00	@	—	—
Red Lead (American).....	Lb.	6 1/2	@	7
Salt Cake (glass-makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	37	@	39
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	65	@	70
Sodium Acetate.....	Lb.	4	@	4 1/2
Sodium Bicarbonate (domestic).....	Lb.	1	@	1 1/4
Sodium Bicarbonate (English).....	Lb.	2 3/4	@	3
Sodium Bichromate.....	Lb.	4 1/2	@	4 1/4
Sodium Carbonate (dry).....	Lb.	60	@	80
Sodium Chlorate.....	Lb.	8 1/4	@	9 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.57 1/2	@	1.62 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	2.40	@	2.45
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	67 1/8	@	7 1/4
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	14 1/4	@	14 1/2
Tin Oxide.....	Lb.	44	@	46
White Lead (American, dry).....	Lb.	5 1/4	@	6
Zinc Carbonate.....	Lb.	8 1/2	@	10
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 3/8	@	6 3/8
Zinc Sulfate.....	Lb.	2 1/4	@	2 3/4

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	42	@	45
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	8 7/8	@	10
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.40	@	6.45
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	56	@	57
Cottonseed Oil (p. s. y.).....	Lb.	9 1/4	@	9 1/2
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	9	@	9 1/2
Lard Oil (prime winter).....	Gal.	96	@	98
Linseed Oil (double-boiled).....	Gal.	50	@	52
Menhaden Oil (crude).....	Gal.	25 1/2	@	27 1/2
Neatsfoot Oil (20°).....	Gal.	98	@	1.10
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2	@	3 3/4
Paraffine Oil (high viscosity).....	Gal.	26	@	28
Rosin ("F" grade).....	Bbl.	4.95	@	5.00
Rosin Oil (first run).....	Gal.	30	@	34
Shellac, T. N.....	Lb.	21	@	22
Spermaceti (cake).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9 1/4	@	9 3/4
Tallow (acidless).....	Gal.	64	@	67
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	39	@	39 1/2

METALS

Aluminum (No. 1 ingots).....	Lb.	22 1/2	@	23
Antimony (Hallet's).....	Lb.	7 3/4	@	8 1/2
Bismuth (New York).....	Lb.	2.10	@	2.15
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	Lb.	14 1/4	@	14 1/2
Copper (lake).....	Lb.	14 3/8	@	14 7/8
Lead, N. Y.....	Lb.	4.32 1/2	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	46.00	@	—
Silver.....	Oz.	59 1/8	@	60
Tin.....	Lb.	40.00	@	44.00
Zinc.....	Lb.	5.22 1/2	@	5 25

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	2.95	@	—
Blood, dried.....	Unit	2.85	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	27.50	@	28.00
Calcium Nitrate (Norwegian).....	C.	2.40	@	—
Castor meal.....	Unit	nominal	@	—
Fish Scrap, domestic, dried.....	Unit	nominal	@	—
Mowrah meal.....	Ton	nominal	@	—
Phosphate, acid, 16 per cent bulk.....	Ton	—	@	7.00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	3.00	@	3.25
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	38.55	@	—
Pyrites, furnace size, imported.....	Unit	0.13 1/2	@	—
Tankage, high-grade.....	Unit	2 75	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

SEPTEMBER, 1913

No. 9

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhenny, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly.

Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

No claims will be allowed unless made within 60 days

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

The Forty-eighth Annual Meeting of the American Chemical Society.....	712
Wood Alcohol.....	712

ORIGINAL PAPERS:

The Microstructure of Steel Castings. By Wirt Tassin	713
Lubrication with Oils, and with Colloidal Graphite. By Charles F. Mabery	717
The Action of Various Substances on Concrete. By Richard K. Meade	723
The Decomposition of Feldspar and Its Use in the Fixation of Atmospheric Nitrogen. By William H. Ross	725
The Leaching of Potash from Freshly Cut Kelp. By A. R. Merz and J. R. Lindemuth	729
A Possible Commercial Utilization of Nelsonite. By William H. Waggaman	730
Quantitative Determination of Rosin in Paper. By C. Frank Sammet	732
Colorimetric Method for Titanium in Iron and Steel. By C. R. McCabe	735
Vanadium in Steel by the Hydrogen Peroxide Color Method. By C. R. McCabe	736
The Determination of Zinc in Treated Ties. By Francis C. Frary and M. Gordon Mastin	738
Hickory Nuts and Hickory Nut Oil. By George O. Peterson and E. H. S. Bailey	739
The Analysis of Maple Products I. An Electrical Conductivity Test for Purity of Maple Syrup. By J. F. Snell	740
The Composition of Different Varieties of Red Peppers. By L. M. Tolman and L. C. Mitchell	747
Some Distinctions between Pepsin and Peptase. By Dr. R. Wahl	752
Determination of Total Formaldehyde in Fumigators and Commercial Solutions. By Jack J. Hinman, Jr.	752

LABORATORY AND PLANT:

An Automatic Pipette. By C. H. McCharles	755
Improved Gooch Crucible Holder. By Lorin H. Bailey	756
Note on Producer Gas Analysis. By James G. Vail	756

ADDRESSES:

The Chemical Industries and the Universities. By Marston Taylor Bogert	757
Depreciation and Obsolescence. By Richard K. Meade	762
The Corrosion of Lead. By Richard H. Gaines	766
Wood Alcohol	768
Some Peculiar Functions of the Retained Expert. By W. M. Grosvenor	772

CURRENT INDUSTRIAL NEWS:

The Catalytic Production of Petrol	774
The Manufacture of Cold-Process Soaps in Egypt	774
The Pulp-Wood Consumption in Canada	774
Some Problems of the Rubber Industry	775
The Exportations of Camphor from Japan, 1910 to 1912	775
"Silit" and Its Applications in the Chemical Industries	775
The Schoop Metallizing Process	776
Recent Activity in the Explosive Pump Art	776
The Alkali Inspector's Report for 1912	779
Wanted: New Uses for Bromine	780
The Radium Market	780
The Manufacture of Copper Wire by Electrodeposition	780
The Melting Points of Elements of Atomic Weight, 48 to 59	780
The Granulation of Slag	780
Some Innovations in the Paper Industry	781
The Gas and Electric Consumption in Greater New York	781
The Consumption of Thorium in the United States	781

SCIENTIFIC SOCIETIES:

Society for Promotion of Engineering Education	781
International Engineering Congress, 1915	782
American Engineers Entertained in Germany	783
William James Evans	783
Mine Sanitation Section of U. S. Bureau of Mines	783

NOTES AND CORRESPONDENCE:

A Criticism of Chemical Abstracts	783
Paints for Indicating the Uses of Pipes	784
On Methods of Analysis of Crude Glycerine	784
What's the Matter with the American Chemist?	785
What's the Matter with the American Chemist?	785
A Rapid Method for the Determination of Fat in Ice Cream	786
Peat Powder as Fuel for Locomotives	786
The Chemical Composition of Cooked Vegetable Foods. Part III.—Correction	786
Paper from Seaweed	786

BOOK REVIEWS:

Chemical Works. Their Design, Erection and Equipment; The Materials Used in Sizing; Fatty Foods, their Practical Examination; Gasanalytische Methoden	786
---	-----

NEW PUBLICATIONS

788

RECENT INVENTIONS

789

MARKET REPORT

790

EDITORIALS

THE FORTY-EIGHTH ANNUAL MEETING OF THE AMERICAN CHEMICAL SOCIETY

To the members who have learned from experience the value of our general meetings no appeal need be made to continue in their attendance. To those who go intermittently or who have not as yet attended, we would emphasize the importance of these meetings and of the Rochester meeting (September 9-12) in particular. Our general meetings afford benefits of several kinds. Most important is the opportunity to meet the foremost men in the chemical profession and to talk over matters of mutual interest. Then there is the discussion of papers which is frequently of more value to us than the papers themselves, and the discussions are not published. Again, the Society visits manufacturing institutions of interest to them, and each city offers something unique. Further, the social features, the get-together sessions, the renewal of friendships, all add their quota of attraction.

The chemist going to the general meeting for the first time is liable to feel himself among strangers. He makes a few friends, meets some men from the old school and gets enjoyment from the meetings, but is apt to think that the trip was hardly worth the cost and is doubtful about going to the next meeting. A mistake is made if this is followed out, for the men deriving the greatest benefits from the American Chemical Society meetings are those who go regularly.

We are about to hold our first annual meeting as a separate society on the plan now in force which puts us on our own feet as an independent organization, standing out as the largest chemical society in the world. Every effort is being made by the Rochester Section to offer attractions which will guarantee an attendance in proportion to the importance of the meeting. Rochester is within easy distance of a large majority of our members and has excellent transportation facilities. Both academic and industrial men will be well cared for, the general meeting being scheduled at the great works of the Eastman Kodak Co. and the sectional meetings at the University of Rochester. Factory excursions will be a special feature covering a field from the production of the instruments used by the chemical profession to works making the most modern application of chemistry to industrial problems. Factories, the duplicates of which do not exist in this country or abroad, will be visited. Social features will be prominent and a good program has been arranged for the ladies.

We urge members to be in attendance the first day, for such a unique program has never been planned for this Society. The general meeting at Kodak Park will be followed by a complimentary luncheon at the Kodak Works and an inspection of the plant, this being the only opportunity of making the inspection. In the evening comes the smoker, full of novelty, amusement and good fellowship. A live committee has been working on this event for months for your benefit.

Let the members of the American Chemical Society descend upon Rochester in unprecedented numbers for the first day, Sept. 9th, and make the forty-eighth meeting the best ever! All will be amply repaid.

WOOD ALCOHOL

Since man began handling fire he has been utilizing dangerous substances to his own good purposes. Also the chemist has discovered many substances and shown how they might be used for the benefit of mankind; he has demonstrated the value of cyanides for extracting gold; how strychnine may serve as a heart stimulant; he has proved the value of phenol as a disinfectant; and how sulfuric acid may be used in multitudinous ways. All these substances are dangerous to handle, in fact many of the commoner reagents used in the hundreds of laboratories and factories are poisons. Were partial facts only presented, it is conceivable that they might assemble themselves in astounding array, which, if not properly interpreted, would serve for a cause of impeachment of the entire chemical profession, whose daily routine is one of handling poisons of all kinds, except for the fact that the chemist is supposed to know his business as well as the substances he handles, and to take some precautions for safeguarding himself and the people working with him. It is a matter of business, even if it presented no humanitarian features.

Our attention has recently been directed to attacks made upon methyl alcohol, the production and sale of which constitutes a legitimate chemical business involving the annual manufacture and use of about 10,000,000 gallons of that substance with a capital investment in this country of about \$12,000,000, an industry which employs over 3,000 working people. We find in current literature, read by the many, assertions made by undoubtedly honest, but overzealous and presumably misinformed persons, or persons not sufficiently informed of the facts to be competent to judge according to proportionality, such as the following: "It is unsafe to burn wood alcohol or use it in any way in a room where the air is close. *The bottle should never be uncorked unless the windows are wide open.*" (Italics ours.) Where would all the nearly 7,000 members of the American Chemical Society be if the latter were really true?

There is no doubt about wood alcohol being a poison if taken internally (although we know of cases, perhaps accounted for by idiosyncrasy, where no evil effects have resulted from drinking it) and if breathed as a vapor in a concentrated form for unusually long periods of time. In fact, nearly a thousand cases of poisoning attributed to wood alcohol (mostly due to drinking it) have been reported in the literature since 1899, the time which marked the advent of such preparations as "Columbian Spirits," "Colonial Spirits," etc.—that is to say, methyl alcohol of a high grade of purity. In 1906, due to a general agitation for a tax-free, denatured ethyl alcohol, hearings were held before the Ways and Means

and the Finance Committees of the Federal Congress. The injurious action of wood alcohol on the general health and eyesight of working people handling it in the industries was strongly emphasized at these hearings by manufacturers employing it, workmen and experts.

The United States and practically every state in the union have specific laws against the sale of wood alcohol as a beverage, or as an addition to beverages. In thickly populated communities the fear of detection is lessened, hence cases of adulteration are more numerous, especially where there is foreign cheap labor. That fact (especially in New York and New Jersey) coupled with a few cases of serious poisoning by wood alcohol in varnishing brewers' vats, which are not properly ventilated, caused the New York State Factory Investigating Commission to look into the wood alcohol situation. The Commission invited Professor Baskerville of the College of the City of New York, then Chairman of the Committee on Occupational Diseases in the Chemical Trades of the New York Section and chemical adviser of the Committee on Occupational Diseases of the New York State Labor Association and now Chairman of the Committee on Occupational Diseases of the American Chemical Society, to make a report on "Wood Alcohol." This report, based on a thorough investiga-

tion of the literature and extensive inspection of works of all kinds where wood alcohol is made and used in various ways, we have been privileged to abstract previous to final publication by the State, which abstract appears elsewhere in this issue. The full report may be secured by writing to the Commissioner of Labor, Albany, N. Y.

Wood alcohol presents a unique case for legislation, not only on account of its general resemblance to ethyl alcohol, but especially on account of the word "alcohol," which has a definite meaning to the chemist, but is more associated in the lay mind with "drink."

Methyl alcohol is used extensively as a valuable solvent and in the manufacture of many important materials. Its legitimate use should not be throttled. The present laws in regard to its use as an adulterant of beverages or in any preparation intended for internal use or external application on the human body are in most states now adequate, but they should be more rigidly enforced. Where inadequate, we trust that reasonable legislation, such as is recommended in the report referred to above, may be enacted. At present, however, we insist upon the rigid execution of the laws as they exist before further encumbering the codes.

ORIGINAL PAPERS

THE MICROSTRUCTURE OF STEEL CASTINGS

By WIRT TASSIN

Received July 23, 1913

INTRODUCTION

This paper deals with the results of some metallographic investigations of steel castings. All of the micrographic work was done in the machine shop on the castings themselves, not on small sections cut from them.

The work was undertaken during the course of what is planned to be a fairly comprehensive study of the relation between structure and physical properties of steel in the mass, and intended for use as a guide by the Inspector and Engineer of Tests.

The present paper gives the results of the work on Tropenas steel castings, and is intentionally made as non-technical as possible.

INFLUENCE OF ANNEALING ON STRUCTURE

A steel casting in the "green," especially when of a complicated shape, is always liable to be under internal strain. In order to relieve these strains annealing is resorted to. This process has a marked effect upon the structure of the metal.

The structure of a steel casting in the "green," *i. e.*, as it leaves the mold, is coarsely crystalline and exhibits to a greater or less degree a regularly arranged network, the meshes of which usually intersect at some angle of an octahedron (Fig. 1). This structure is known as "ingotism."

Heat-treating such a casting breaks down this original crystallization and, if properly carried out, effaces it. Thus in a properly annealed casting the coarse crystal-

line structure gives place to another which is fine-grained and of a uniform distribution (Fig. 2).

The degree to which this change takes place is limited by the temperature reached, its uniformity, the time that it is maintained, the rate of cooling, and the size and shape of the casting.

Given the proper temperature, but let the time be too short to permit of a complete re-arrangement, the structure will be analogous to that seen in Fig. 3, in which the original structure is readily traced by the parallel grouping of the new crystallization. With a still shorter time period there is only a partial re-crystallizing, and more or less of the original network is visible (Fig. 4).

Let the time be long enough, but the temperature be too low, there will be again a partial re-grouping with more or less of the original crystallization present (Fig. 5).

Let the temperature be right but the time period be too long, all traces of the original structure will be destroyed, but in place of the fine granular structure seen in Fig. 2 there will be a much coarser one (Fig. 6) characterized by the large-sized areas of a certain kind.

Let the temperature be too high and the increase in size of certain areas become marked (Fig. 7).

RELATION OF STRUCTURE TO PHYSICAL PROPERTIES

The character of the structure bears a relation to the physical properties of the metal in the casting, the finer the grain, the more uniform its distribution and the freer it is from occluded foreign matter as slag, sulfide, oxide, etc., the better will be the physical properties.

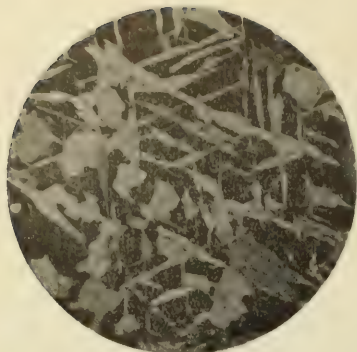


FIG. 1. $\times 65$

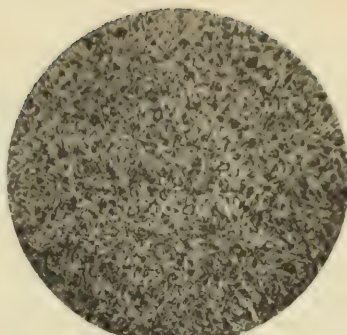


FIG. 2. $\times 65$

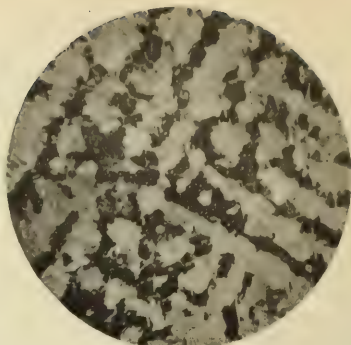


FIG. 3. $\times 65$

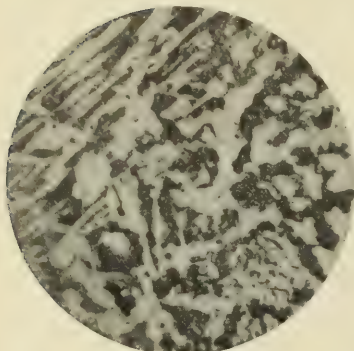


FIG. 4. $\times 65$

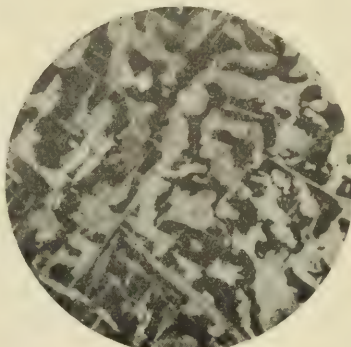


FIG. 5. $\times 65$

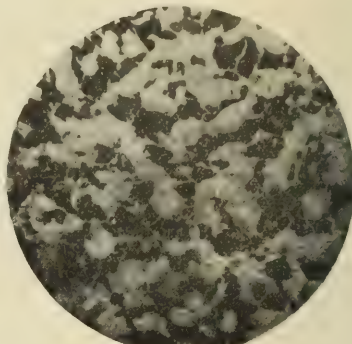


FIG. 6. $\times 65$

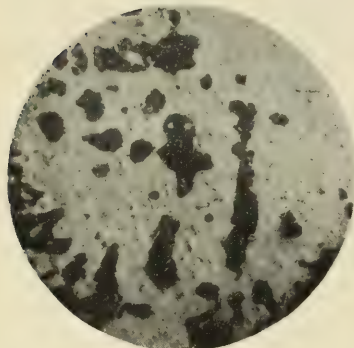


FIG. 7. $\times 65$

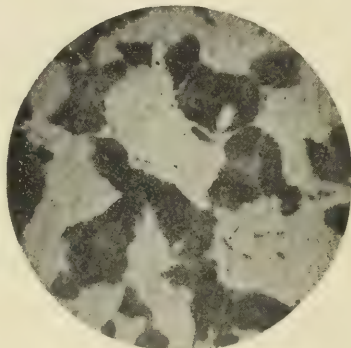


FIG. 9. $\times 150$

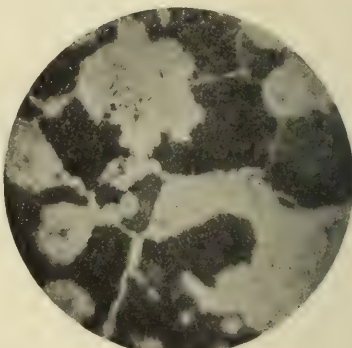


FIG. 10. $\times 150$

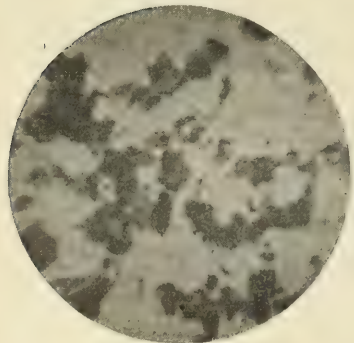


FIG. 11. $\times 150$

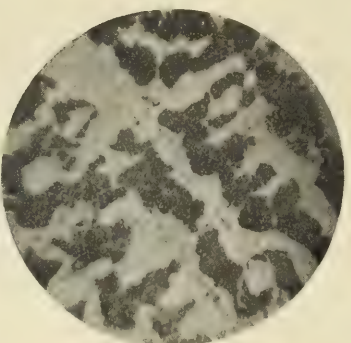


FIG. 12. $\times 150$

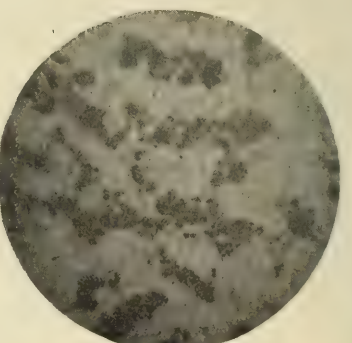


FIG. 13. $\times 150$

The following examples (Figs. 9-15) give the type of the structures as obtained from four or more different places on each casting. The physical values given were obtained from a coupon 5.5" X 3.5" X 1.5" cast on and part of the casting and placed, it was believed, so as to represent neither the best nor the worst of the casting but to give the average of the piece.

The castings were spot polished, etched and photographed in the shop with the portable metallographic outfit (Fig. 8) described by the writer in *Metallurgical and Chemical Engineering*, 11, 56-8.

All the photographs are of the same amplification

with a low resistance to shock and to suddenly applied loads. The microstructure of such castings commonly shows the presence of slag, sulfides, oxide and other impurities. Typical illustrations of this are to be seen in Figs. 16 and 17.

The following examples (Figs. 18-20) give the type of the structures as obtained from four or more places on the casting. The physical values were obtained from coupons cast on and part of the casting.

The photographs are of the same amplification with a magnification of 150.

These impurities play an important part as a cause

TABLE I

Mark	Tensile	Yield point	Elong.	Red	Analysis				
					C	Mn	Si	S	P
Fig. 9.....	71,356	38,832	23.75	34.72	0.31	0.63	0.27	0.071	0.044
Fig. 10.....	70,991	38,489	19.25	23.26	0.31	0.61	0.29	0.073	0.043
Fig. 11.....	70,791	39,502	16.75	18.00	0.31	0.59	0.29	0.072	0.040
Fig. 12.....	70,620	39,216	14.00	15.75	0.37	0.60	0.29	0.069	0.040
Fig. 13.....	69,980	39,205	12.00	14.50	0.31	0.60	0.28	0.069	0.043
Fig. 14.....	72,000	33,000	10.75	11.50	0.31	0.67	0.28	0.065	0.040
Fig. 15.....	73,000	40,000	8.50	10.00	0.31	0.62	0.28	0.054	0.044

with a magnification of 150 and are directly comparable with one another.

The castings were made by the same process but in widely separated heats.

of failure. Thus in Figs. 21 and 22, from castings which have failed in service, and which are areas some distance away from the point of actual rupture, it will be noted that there are minute cracks in the grain

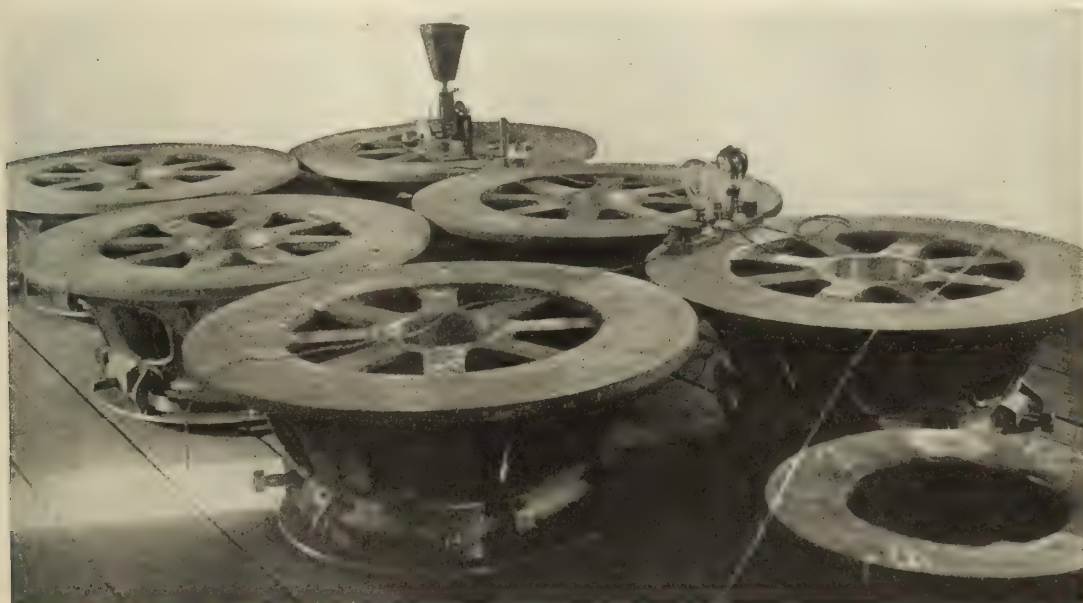


FIG. 8

It will be noted that these structures are all referable to one or the other of the types previously shown as resulting from the conditions of annealing.

Annealing, however, is not the only factor that influences the physical properties, for, given good annealing practice, it is not infrequent to find a casting

and that these cracks start in and follow the line of the impurities. In Fig. 23 the cause of the rupture is clearly indicated.

CONCLUSION

One, more, or all of the several structures here illustrated may be found in any one steel casting.

TABLE II

Mark	Tensile	Yield point	Elong.	Red.	Analysis				
					C	Mn	Si	S	P
Fig. 18	70,000	36,500	12.50	16.25	0.35	0.65	0.29	0.070	0.040
Fig. 19	71,400	37,480	10.50	13.25	0.38	0.68	0.29	0.065	0.042
Fig. 20	70,900	35,150	13.75	17.40	0.32	0.64	0.28	0.071	0.045

If, as is generally the case, the coupon be gated to the casting, or be cast on the heavy part, or on the drag, it will represent the best values of the metal, when,

the microstructure of the casting and its physical value.

It can be shown that a casting may be spot polished

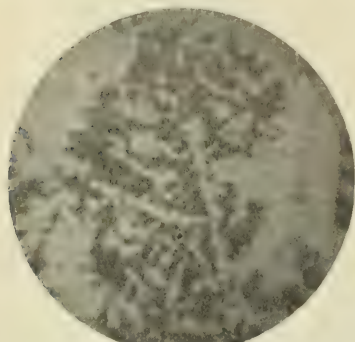
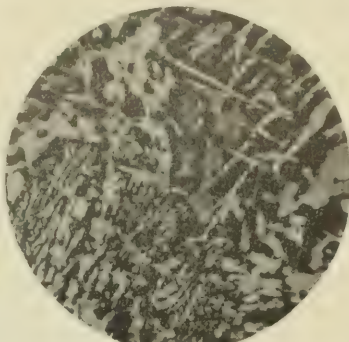
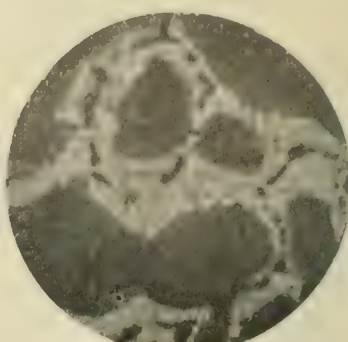
FIG. 14. $\times 150$ FIG. 15. $\times 150$ 

FIG. 16

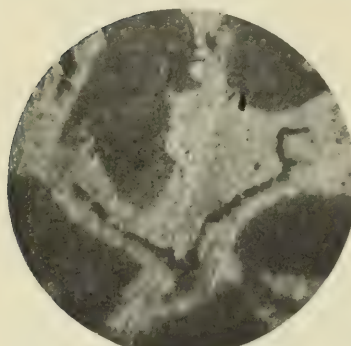
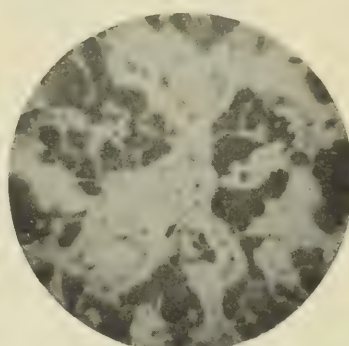
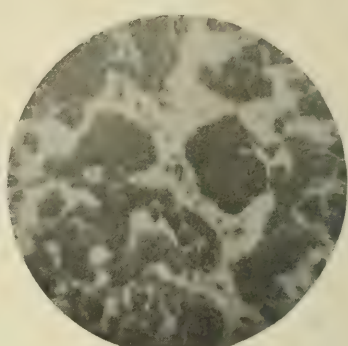
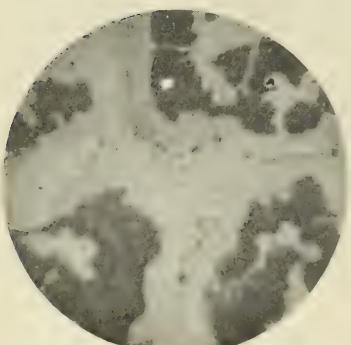
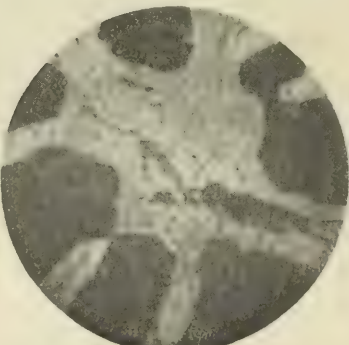


FIG. 17

FIG. 18. $\times 150$ FIG. 19. $\times 150$ FIG. 20. $\times 150$ FIG. 21. $\times 150$ FIG. 22. $\times 150$

in fact, the average value of the casting may be such that it will have but little resistance to sudden strains.

It has been indicated that there is a relation between

in eight or more different places with but little, if any, more expense and time than it takes to prepare a standard test bar.

It follows that, given sufficient experience and a set of standards, the metallographic method will give information that cannot be obtained conveniently by

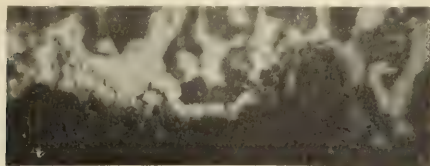


FIG. 23.

any other manner of test. It becomes, therefore, an additional safeguard in the inspection of important castings.

1423 R St., N. W.
WASHINGTON, D. C.

LUBRICATION WITH OILS, AND WITH COLLOIDAL GRAPHITE

By CHARLES F. MABERY

Received July 14, 1913

In a paper¹ published three years ago, an account was given of some results on the comparative efficiency in lubrication of oil lubricants, and oils carrying colloidal² graphite. It appeared in all the tests therein described that a lower coefficient of friction was given by the use of graphite than by the use of oils alone, that oils supported a much greater pressure with the aid of graphite, and especially that the graphite film was capable of sustaining the friction of a heavy pressure for a long period after the supply of lubricant was shut off. Much attention has since been given to various features of lubrication with colloidal graphite, especially in attempts to ascertain the actual economy of its use in replacing oil lubricants. The observations to be described in this paper present high economic efficiency and a remarkable durability of a graphoid surface. (For a definition of this term see page 722.)

It has long been felt that lubrication with oils under heavy pressures is an artificial system, for the friction is supported by a thin film of oil which must separate completely and continuously the bearing surfaces. If this film be in the least broken, even in minute places, there will be a catch between the metal surfaces with greatly increased friction, as shown by higher temperatures as well as by higher coefficients. This uncertainty in oil lubrication depends on an inherent weakness of the hydrocarbons which constitute the main body of petroleum lubricants, assuming that they have been separated from the crude oil without decomposition in the process of refining; they are few in number, and members of a limited series represented mainly by the general formulas C_nH_{2n} , C_nH_{2n-2} , and C_nH_{2n-4} . The limited number of hydrocarbons in these series is shown by the fact that they may be collected within comparatively narrow limits of temperature during distillation, provided, of course,

that decomposition is avoided. The stability of these hydrocarbons diminishes in a somewhat regular manner with the increase in complexity of composition, until a point is reached where the oils cannot be distilled without cracking even *in vacuo*. This variation in stability appears in their use as lubricants, especially under irregular conditions of friction and temperature. But so long as the temperature is kept down and the bearings have a properly even surface, the hydrocarbons of suitable viscosity serve as durable lubricants. Under uneven conditions of friction they are liable to immediate decomposition even to carbonization. This complete decomposition is frequently observed especially in the extremely variable conditions of automobile lubrication. In fact the demands of modern locomotion with unprecedented high speeds, such as in automobile racing, uneven loads, and the variable changes of highway traffic, have reached a burden of lubrication that no oils, mineral, vegetable, or animal, are capable of supporting. Carbonization in automobile lubrication is an occurrence of common observation, and oils are rated on the basis of a so-called carbon test, which shows certain differences in stability depending on a difference in the composition of the oils, and also on the method of refining. No oils can withstand the irregular operations of certain automobile practice without carbonizing to a greater or less extent.

Lubrication with oils is based on the quality of oiliness, or greasiness that is inherent in the hydrocarbons poorer in hydrogen mentioned above. It is not strictly defined by viscosity as ordinarily determined. While the molecules have a certain freedom of motion within the body of the oil attended with a consequent inherent friction, they have also an attraction for external surfaces on which they may form an attachment, but preserving their continuity and freedom of motion even under high pressures and high speeds, thus forming, under constant conditions, a continuous and a durable film.

Engler¹ in referring to oil lubricants stated that "Das Schmiermittel par Excellence" is not known, but that for every special use a lubricating oil must be selected on the basis of its viscosity; that since for variable combinations of pressure and speed, there is no definite standard, the viscosity must be determined for any set of conditions in practical operation. It may be said further that viscosity as ordinarily determined is not always reliable for determining the quality of a lubricating oil for any stated condition, for the reason that it is possible to prepare an oil lubricant by compounding a heavy distillate with a lighter one, leaving out the middle fraction, in such a manner as to give any viscosity desired as determined by the viscosimeter. But in the use of such a lubricant there is a tendency of the lighter constituents to creep and evaporate, leaving the heavy constituents between the bearing surfaces. It is evidently possible to determine the presence of any considerable amount of the lighter constituents by determining the flashing point of the oil, but this test is scarcely sufficient to

¹ THIS JOURNAL, 2, 115; *Journal of the American Society of Mechanical Engineers*, January, 1910.

² At the time of the former publication the term "deflocculated" was used to designate this form of carbon which had been found to be altogether different in its properties from the other well known forms. Further study demonstrated its colloidal quality.

¹ *Das Erdöl*, Leipzig, 1912, p. 83.

indicate with precision the presence of such proportions of the lighter constituents as may be used to give the desired viscosity. A more accurate means of control is distillation which, if conducted in *vacuo*, should show the smallest proportion of lighter oils. A further aid from a practical point of view, and one that is highly desirable if properly conducted with reference to factory use and conditions, is the trial of an oil on a suitable bearing provided with the means for ascertaining the coefficient of viscosity and for reading temperatures.

On account of the inherent weakness in oil lubricants referred to above, the need is evident of a solid lubricant capable of equalizing the inequalities of the metal surfaces and of such adequate lubricating quality as to avoid intermolecular friction. Of all known materials the substance graphite alone possesses the qualities of a normal lubricant. In its ordinary natural condition it is not possible to mechanically subdivide it so completely that it can penetrate the fine interstices of metallic surfaces and at the same time form a persistent coherent lubricated surface; but in a form of complete purity, free from the mineral constituents of natural graphite and in a condition of minute subdivision, such as is formed by the conversion of Acheson's electric furnace graphite into its colloidal condition, there is available a solid lubricant that fulfills the requirements of economic lubrication. It is so finely divided that it readily permeates metals and by reason of its unctuous quality its own friction is reduced to a practically negligible quantity, thus escaping the internal friction of oil lubricants that is an important factor in the losses of power in factory operation.

The action of colloidal graphite is two-fold: its permanent suspension in oil as oildag or in water as aquadag renders it capable of convenient application and it invariably reduces the viscosity of the oil as a medium of application as shown by many tests with a great variety of oils; its greatest value, however, depends on its readiness to form a graphoid condition on bearing surfaces. It is only necessary that it be suspended in a suitable medium free from any kind of electrolyte to give the finely divided particles freedom of motion. When evenly spread in an oil medium over a bearing surface such, for example, as a Babbitt bearing of the proper quality, the colloidal particles immediately enter the fine metallic interstices and accumulating form a combination somewhat analogous to an amalgamated surface, which needs only to be properly renewed by regular additions of the lubricant to present a bearing surface capable of supporting any reasonable pressure and with the lowest friction that it is possible to obtain.

In the description of the Carpenter machine on which the tests presented in this paper were made, in the former paper referred to above, the necessity of using a hard Babbitt bearing was mentioned. The condition of the journal and of the bearing have been more carefully considered in the recent work, especially with reference to the hardness of the Babbitt, the smoothness of surface, and the even distribution of the

lubricant by the grooved bearing. It is evident that observations of this nature are altogether relative, especially as it is practically impossible that independent bearing surfaces are precisely in the same condition. By the use of a standard lubricant it is of course possible to compare tests made under different conditions.

In the work herein described an especially hard Babbitt was selected, and the bearing surfaces were milled down to true contact in the beginning, and by long-continued use were worn to as extreme a condition of fine smoothness as it is possible to obtain by ordinary mechanical operation. Comparing the extremely low coefficients and temperatures recently obtained with those formerly presented, the difference in the condition of the bearings is evident. While these conditions are necessary in showing small differences of friction, evidently no such strict adherence is necessary in factory operation, although the more closely they are applied in practice the less will be the loss in power. Under any reasonable conditions of operation the use of colloidal graphite as lubricant is certain to reduce the friction very materially and to serve as an important economic element in factory maintenance.

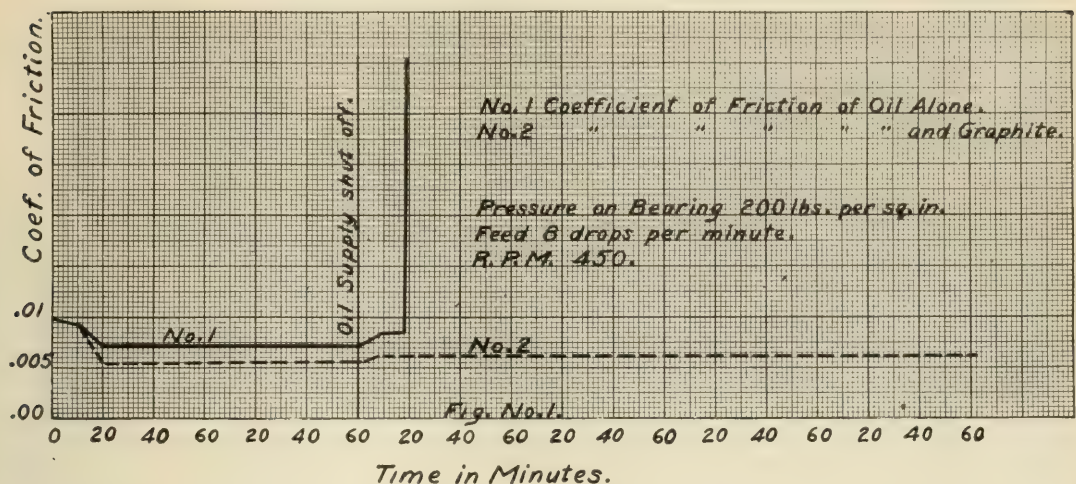
For the purpose of ascertaining with greater precision than formerly the influence of colloidal graphite in reducing friction, observations were made under a variety of conditions, more especially for the purpose of comparing its superior economy over that of oil lubricant. First in the series of tests one of the best automobile lubricants was selected for a test of its frictional capacity alone, and then with different percentages of graphite. The oil was allowed to run from the cup at the rate of eight drops per minute for two hours, with a thermometer inserted in a hole in the bearing for the purpose of reading the temperatures. The pressure selected was 200 lbs. per sq. in. or a total of 1500 lbs. The speed was 450 revolutions per minute (r. p. m.).

Fig. 1 shows the coefficients of friction extending through the period of the test, two hours, and also that the oil film broke seventeen minutes after the supply was shut off.

It should also be mentioned in connection with this observation that a supply of eight drops per minute of the lubricant is the minimum amount of this oil that will support the friction of this pressure under these conditions. This was determined in another experiment, wherein the flow of oil was reduced to six drops per minute; the oil film broke soon after the test was started showing that this quantity of oil was insufficient, a result precisely similar to what was observed in the work three years ago with the same oil and with other oils. The low coefficient of friction in this test is worthy of note, and also its evenness after normal conditions were established, and until the oil film broke.

Fig. 1 also presents the curve for the same oil carrying 0.35 per cent graphite under the same elements of pressure, speed, and supply of oil to the bearing. The low coefficient of friction is apparent which, with

Chart for Motor Oil with and without 0.35% Colloidal Graphite

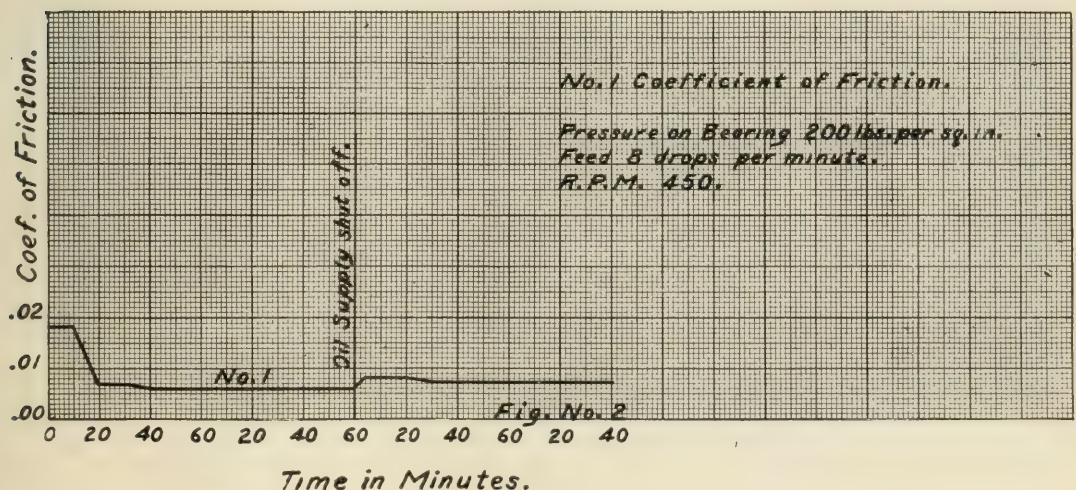


a corresponding lower temperature, indicates clearly the influence of the graphite in reducing the viscosity of the oil, but the observation of especial interest in this test is the permanence of the graphoid surface after the supply of lubricant was discontinued. It appears that this surface supported a pressure of 200 lbs. per sq. in. with an extremely low and even coefficient of friction that continued unchanged during five hours and would probably have continued much longer.

For the purpose of ascertaining whether larger or

pressure of 150 lbs. per sq. in. The results of this test are not essentially different from those of Fig. 2 with 0.35 per cent graphite, although the coefficients are somewhat lower with the larger percentage. There is therefore little to choose between these percentages in establishing the initial graphoid surface; but as will be shown later a suitable surface can be permanently maintained when it is once established by a much smaller addition of lubricant, whether it be used as a smaller percentage of graphite, or by a diminished supply of oil carrying the normal proportion.

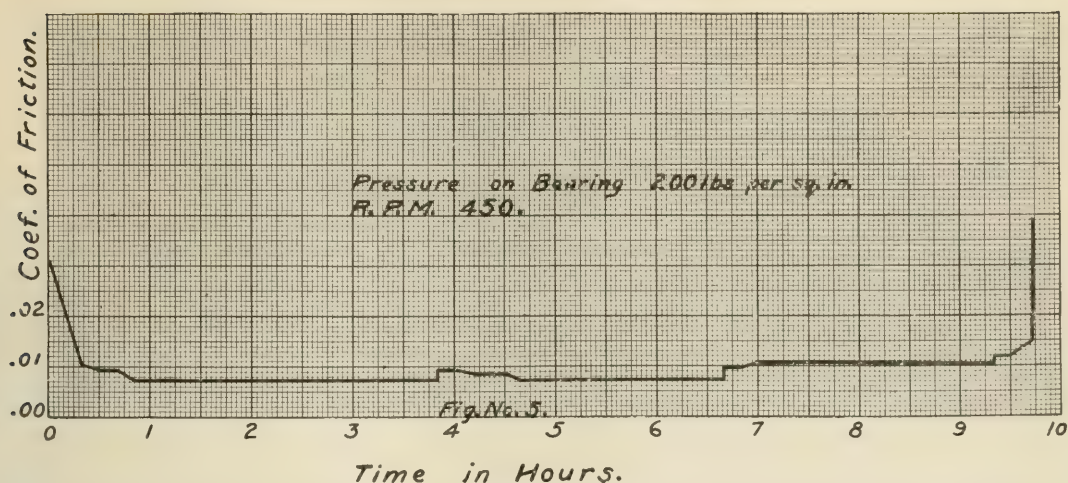
Chart for Motor Oil with 0.25% Colloidal Graphite



smaller percentages of graphite are advantageous, several runs were made with lubricants carrying 0.5 per cent and smaller percentages to 0.1 per cent, but neither of these extremes were satisfactory. Fig. 2 presents the results as to coefficient with the lubricant carrying 0.25 per cent of graphite under a

For the purpose of ascertaining the minimum amount of graphite that will maintain a graphoid condition when once formed on the bearings, a series of tests were made gradually reducing the supply of lubricant all under the same conditions of pressure and speed. Fig. 3 gives the curves after the flow of

Chart for Endurance Test on Colloidal Graphite Alone

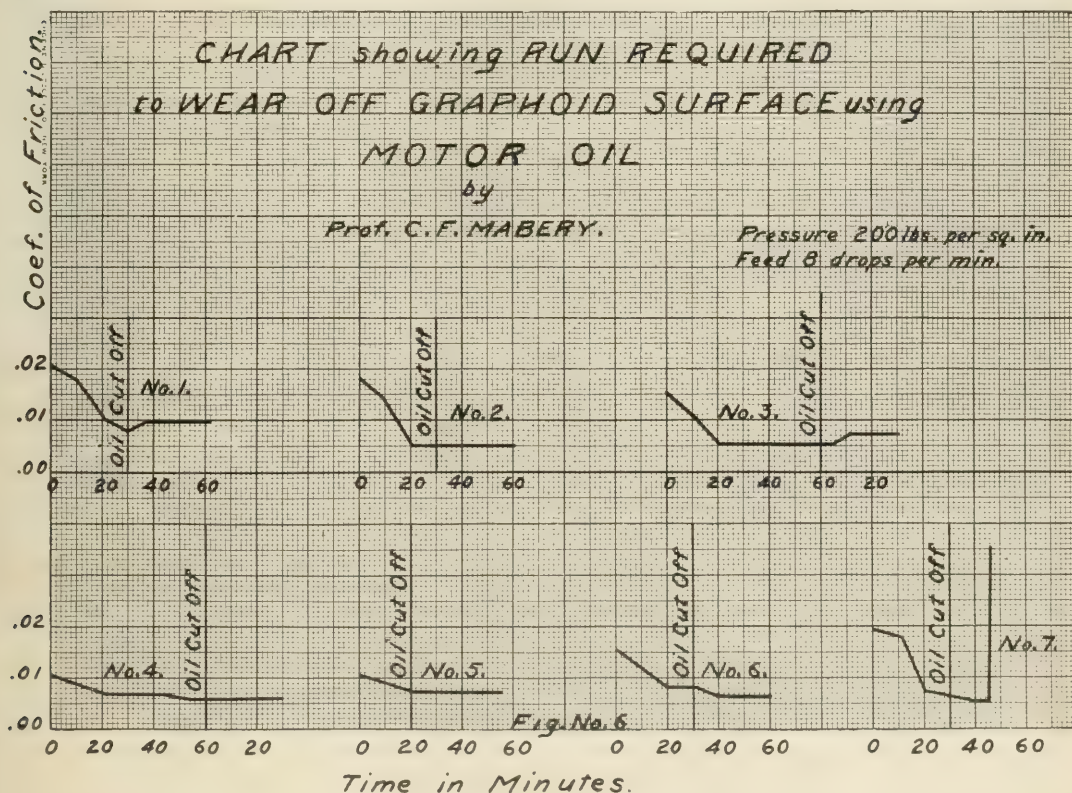


have maintained the graphoid surface, but this flow was practically at the lowest point where it could be accurately measured from the oil cup.

It appears, therefore, that the same result in lubrica-

tion was shown that a flow of eight drops per minute is the minimum supply of oil alone that will support the friction under these conditions.

For the purpose of testing still further the quality of



tion is obtained by the use of one-sixteenth of the quantity of oil that is necessary to maintain the same lubrication without the use of colloidal graphite; for

the graphoid surface, at the end of the last test the flow of lubricant was suspended and the machine allowed to run until the bearing caught. The

results of this test are shown in Fig. 5 where it appears that the pressure was supported for nearly ten hours and with a coefficient only slightly higher than in the preceding tests. It should be borne in mind that a break in the continuity of the lubricated surface is indicated suddenly by a great rise on the friction arm and it is caused by the first point or section however minute wherever the graphite becomes worn through, yet there may still be a large section of lubricated surface. This appeared in the next experiment.

The manner in which colloidal graphite is able to support such heavy pressures with low friction has already been explained. After the metallic surface becomes completely saturated with graphite evidently without renewal continued friction would be necessary to remove it completely. It therefore seemed of interest to ascertain how readily it could be removed. A series of runs were made on the same surface after it broke in the last test, with the addition of oil alone at the rate of eight drops per minute, to determine just the point where the graphoid surface could no longer assist in lubrication. In each of the runs the oil was allowed to flow for thirty minutes, and the bearings were then carefully wiped. Fig. 6 shows the effect of the graphite in assisting the oil lubrication without change during six runs, and also that it became exhausted and broke in the seventh run showing that altogether approximately three and one-half hours were required to wear off the graphite until it was no longer an aid in lubrication.

A GRAPHOID SURFACE AND THE CONDITIONS OF ITS FORMATION

In the former paper on this subject¹ the effect of colloidal graphite (then referred to as a "deflocculated form") appears the following statement: "One of the most characteristic effects is that of a surface-evenner, by forming a veneer, equalizing the metallic depressions and projections on the surfaces of journal and bearing." After four years experience with graphite lubrication it appears that the former explanation falls short of defining the intimate relation of colloidal graphite to metallic bearings. No doubt in building up the graphoid surface the entire depressions and projections are saturated with graphite which doubtless enters into a closer state of combination with the metallic surface than that merely of a mechanical veneer.

In the use of colloidal graphite as a lubricant it appears that by reason of the tenuity or fineness of its particles, it is capable under the conditions of lubrication of penetrating the porous surface of metals, and coming into such close contact in their intermolecular structure, of approaching a condition of graphitic combination. It then continues to accumulate until a continuous saturated surface is formed, which extends equally over the depressions and protuberances if the bearing is not in the best condition of smoothness; but in its best condition the graphoid surface formed seems to be nearly frictionless.

Since this relation of metal and carbon is not de-

fined by any term now in use, the word *graphoid* used above may serve to distinguish it from the term *film* that expresses the state of an oil lubricant on a bearing surface.

As to the greater efficiency of the graphoid surface over an oil film under any conditions of lubrication there seems to be no question. It all depends on establishing the conditions whereby this surface may be readily formed. An oil medium in which the colloidal graphite is permanently suspended can evidently carry it to any form of bearing surface that needs lubrication. Whatever the condition of the metallic bearing the graphite soon combines with it, and the smoother the surface the more readily will a continuous graphoid surface be formed. In all tests it has appeared that the internal friction of an oil is diminished by colloidal graphite, although its larger effect is altogether independent of oils except as a medium of application. After a graphoid surface is formed only a small continuous addition is necessary to replace the wear which, as shown in the tests, reduces the consumption of oil to a small fraction of what is necessary in the use of oil alone. While eliminating the internal friction of oils and rendering viscosity of secondary importance, the graphoid surface is capable of taking care of light and heavy pressures equally well and with a minimum loss of power.

RELATION OF COEFFICIENT OF FRICTION AND VISCOSITY TO TEMPERATURE

Since the curves for temperatures were found to follow closely those of friction practically unchanged, it was not thought necessary to plot them. In all the observations described in this paper, it was observed that the temperature gradually increases with the duration of the test until it reaches a practically constant value not exceeding 65° F., and that for the most part the temperatures were considerably lower. It appears that the friction generates a certain amount of heat until it reaches a normal which is practically constant, and that beyond this point the increase if any is so slight that it is dissipated. In general the lower the coefficient of friction, the lower will be the temperature. This is shown in Fig. 1, where the temperature and the coefficient for oil alone were considerably higher than those for oil carrying 0.35 per cent graphite. It also appears in the other charts especially in the endurance tests, with a small supply of oil. This is doubtless explained, in part at least, by the internal viscosity of the oil which is of course less with the smaller supply of oil aided by the graphite, and it demonstrates a superior quality of the graphoid condition over an oil film, in eliminating practically internal viscosity.

AUTOMOBILE LUBRICATION

There is probably no variety of lubrication in which colloidal graphite shows its economic value to better advantage than in reducing the friction on automobile bearings. On the Babbitt bearings of the cylinder shaft it readily forms a graphoid surface that wears indefinitely, and the self-lubricating quality of this surface reduces friction to the smallest possible value.

¹ Loc. cit.

It eliminates also any possibility of heating due to an irregular flow of oil. In the wide and sudden variations of highway automobile traffic the bearings are often subjected to greater strain than an oil film can stand, but not a graphitized surface when once well formed. Such protection from undue wear and sudden strains that cannot be avoided in highway locomotion add greatly to the safety and length of service of the finely adjusted mechanism. Assuming properly selected materials in construction, no doubt the most uncertain element in the proper operation and in the economic durability of an automobile is the friction of its moving parts. Its sure control protects the mechanism of the moving parts and materially reduces the expense of operation.

CASE SCHOOL OF APPLIED SCIENCE
CLEVELAND, OHIO

THE ACTION OF VARIOUS SUBSTANCES ON CONCRETE¹

By RICHARD K. MEADE

The following experiments on the action of various substances on concrete were begun some five or six years ago, about the time that the agitation over the destruction of concrete by the alkaline waters of the West was first started and was undertaken not only to see if such action was really likely to take place but also to determine which of the salts ordinarily found in ground waters were the cause of such destruction.

ANALYSIS AND TESTS OF THE CEMENT EMPLOYED

Silica.....	20.20
Oxide of iron.....	2.50
Alumina.....	6.96
Lime.....	62.40
Magnesia.....	3.01
Sulfur dioxide.....	1.60
Loss on ignition.....	2.38

PHYSICAL TESTS

Soundness—Steam O.K.	Cold water O.K.
Boiling O.K.	Air O.K.
Fineness—Passing No. 100.....	94.3%
Passing No. 200.....	97.8%
Setting Time—Initial set—2 hrs. and 15 min.	
Final set—6 hrs. and 30 min.	
Tensile Strength—1 day neat.....	315 lbs.
7 days neat.....	765 "
7 days sand.....	245 "
28 days neat.....	876 "
28 days sand.....	340 "
3 mos. neat.....	885 "
3 mos. sand.....	415 "
6 days neat.....	855 "
6 days sand.....	435 "
1 yr. neat.....	890 "
1 yr. sand.....	510 "

The salts usually found in the so-called "alkali waters" of the West are also those which occur in sea water and are those present in largest amounts in many spring and river waters. They are sodium chloride, magnesium sulfate, calcium sulfate, sodium sulfate and sodium carbonate. In order to test the effect of solutions of these substances on cement mortars, a sample of normal Lehigh Valley cement was selected and from it a large number of sand briquettes were made.

¹ Read at the Sixteenth Annual Meeting of the American Society for Testing Materials, Atlantic City, June 26, 1913.

All briquettes were made from a mixture of one part cement and three parts standard Ottawa sand. They were allowed to harden 28 days in air and then immersed in a solution of the salt. The briquettes were piled in such manner that the solution had access to almost their entire surface.

The solutions in all cases except that of the calcium sulfate, which was a saturated solution, were made up of one part of the salt to 100 parts of water, to form practically a one per cent solution. At first the solutions were changed every few days, but after the first month the solutions were changed weekly and after the first year less often. The results obtained are given in the table below:

ACTION OF VARIOUS SALTS ON CEMENT MORTARS

Age in air.....	0 days	7 days	28 days	3 mos.	6 mos.	1 yr.	2 yr.
Age in the solution.....							
TENSILE STRENGTH							
In MgSO ₄	219	268	272	287	196	Disinte- grated	Disinte- grated
In MgCl.....	219	245	300	315	202	115	
In CaSO ₄	219	227	300	334	314	209	"
In Na ₂ SO ₄	219	257	334	354	378	271	141
In NaCl.....	219	236	268	299	287	310	325
In Na ₂ CO ₃	219	225	277	324	320	337	360

First, it should be remembered that the 28-day strength of briquettes kept in air is much less than that of those kept in water. As will be seen from the results given in the table, the sulfates have a marked action on concrete which seems to be most apparent in the case of the magnesium salt. The action of magnesium sulfate on cement mortars has been discussed quite voluminously of late, and I will not go into it to any length in this paper beyond the fact that we carefully analyzed the affected portion and the unaffected portion of a sand briquette which has been stored in a solution of magnesium sulfate. These analyses follow:

Percentages	After immersion		
	Before immersion	Unaffected portion	Affected portion
Silica.....	75.12	73.96	60.40
Oxide of iron.....	0.52	0.60	0.30
Alumina.....	1.15	1.30	0.64
Lime.....	14.80	14.50	14.21
Magnesia.....	0.70	1.66	3.64
Sulfur trioxide.....	0.33	0.83	5.78
Loss on ignition.....	7.02	7.14	14.97

The large increase in the magnesia and sulfur trioxide and the decrease on the oxides of iron and alumina indicate the elements which react with each other. The loss in silica may be due to chemical action also, but as the surface of the briquettes was very much attacked and the sand grains could be scraped away with the finger, I am inclined to think that the lower silica in the disintegrated portion is probably due to mechanical causes rather than chemical action.

It will be noted that in almost all cases the first effect of the solution was to increase the strength of the briquettes and that signs of disintegration in no cases became evident until after a period of three months in the solution.

Some of the briquettes were even boiled in a 5 per cent solution of magnesium sulfate for several days and in all cases the briquettes were much stronger

after boiling than they were before and fully as strong as briquettes boiled in pure water, showing how slow the action of the sulfates is.

The briquettes which failed were much swollen and presented much the appearance of a baked potato which had burst its jacket.

Various authorities have proposed at different times the use of divers ingredients in concrete exposed to sea water with a view to reacting with the salts of the latter to form insoluble compounds which would protect the concrete. Most persistently suggested of these are the salts of barium which form with sulfates insoluble barium sulfate. I tried both barium chloride and barium carbonate. These were ground very finely and mixed with the cement. I employed 2 per cent of barium chloride with the cement and also 2 per cent and 5 per cent of barium carbonate, respectively. Sand briquettes were made from these mixtures and the test pieces stored in a magnesium sulfate solution containing 10 grams of the salt to the liter. My results follow and, as will be seen, none of these compounds arrest in any way the destruction:

ACTION OF MAGNESIUM SULFATE ON CEMENT MORTARS CONTAINING BARIUM COMPOUNDS

Age in air..... Age in 1 per cent $MgSO_4$ solution.....	14 days					
	0 days	7 days	28 days	3 mos.	6 mos.	1 yr.
TENSILE STRENGTH OF BRIQUETTES CONTAINING						
2 per cent $BaCl_2$	181	...	213	306	265	146
2 per cent $BaCO_3$	115	221	246	311	204	Disinte- grated
5 per cent $BaCO_3$	166	257	346	346	274	"

Some years ago an English chemist suggested the use of finely ground burnt red brick as an admixture for concrete which was to be used in sea water. After reading this paper it occurred to me that the resistance to sea water claimed for high iron cements might be due to the presence of oxide of iron in the cement. I, therefore, had sand briquettes made up containing oxide of iron in various forms and conditions, *viz.*, red or ferric oxide, magnetic oxide of iron, venetian red (an impure oxide of iron made from low-grade iron ores, so-called "paint ores" of the Lehigh District) and finely ground red brick, using 5 per cent of the weight of the cement of these in each case and placing the briquettes in a 1 per cent solution of magnesium sulfate. The results follow:

ACTION OF MAGNESIUM SULFATE ON CEMENT MORTARS CONTAINING IRON OXIDES, ETC.

Age in air..... Age in solution.....	14 days					
	0 days	7 days	28 days	3 mos.	6 mos.	1 year
TENSILE STRENGTH OF BRIQUETTES CONTAINING						
5 per cent ferric oxide....	218	275	310	355	310	125
5 per cent magnetic oxide..	225	280	340	340	280	105
5 per cent venetian red..	165	225	300	345	215	Disinte- grated
5 per cent brick dust.....	970	220	275	310	205	"

As will be seen, the additions of iron compounds are in no way beneficial to cements to be employed in sea water.

I next tried waterproofing the mortar on the theory that if the circulation of water through the pores of the mortar could be stopped no chemical action could take place. I employed for this purpose both a high

calcium and a magnesium hydrated lime, road oil as recommended by Page, a mixture of solution of silicate of soda and fish oil (a well-known waterproof compound) and lime soap (the basis of many waterproofing compounds). I also tried dipping the briquettes first in a hot solution of soap and then in one of alum (Sylvester's Process). The result of sand briquettes made from these mixtures and stored in magnesium sulfate solution (10 grams to the liter) will be found below:

ACTION OF MAGNESIUM SULFATE SOLUTION ON WATERPROOFED(?) MORTARS

Age in air..... Age in 1 per cent magnesium sulfate solution.....	14 days					
	0 days	7 days	28 days	3 mos.	6 mos.	1 year
TENSILE STRENGTH OF BRIQUETTES CONTAINING						
15 per cent hydrated lime (Ca).....	215	215	315	245	200	120
15 per cent hydrated lime (Mg).....	215	225	320	260	245	105
10 per cent road oil.....	165	200	210	260	210	140
2 per cent lime soap.....	185	210	250	275	230	180
2 per cent oil-silicate of soda	160	200	245	260	225	165
Treated with alum and soap.	220	235	275	265	215	185

It will be noted that while the disintegration is evidently taking place in these test-pieces, all of these compounds seem to arrest it to some extent at any rate and in the case of the lime soap this is quite marked.

I also investigated the action of magnesium sulfate solution on cements high in silica. For this purpose a sample of commercial cement high in silica and low in alumina and one low in silica and high in alumina were selected and sand briquettes were made of this and immersed in a solution of magnesium sulfate containing 20 grams to the liter, or practically a 2 per cent solution. The cements selected had the following analyses:

Percentages	Low-alumina cement	High-alumina cement
Silica.....	23.24	19.86
Iron oxide.....	2.25	2.56
Alumina.....	5.03	7.60
Lime.....	63.55	63.12
Magnesia.....	3.05	3.10
Sulfur trioxide.....	1.51	1.66

As will be seen by the following results, the low-alumina cement resists the action of magnesium sulfate much better than the high-alumina one:

ACTION OF MAGNESIUM SULFATE SOLUTION ON HIGH- AND LOW-ALUMINA CEMENTS

Age in air..... Age in solution.....	14 days					
	0 days	7 days	28 days	3 mos.	6 mos.	1 yr.
High-alumina cement.	242	318	404	402	230	Disintegrated
Low-alumina cement..	225	307	430	476	472	500

In the above experiments both cements were commercial cements, but the high-alumina cement when received was not quite so finely ground as the other one, so it was ground to practically the same degree of fineness in a small jaw mill (or to 86.2 per cent passing the No. 200 sieve) so that the fineness of the two samples might, in no way, influence the results. Both these cements were made from cement rock and limestone.

In connection with the use of concrete for mine props, where it is often exposed to the action of dilute solutions of sulfuric acid, the following experiment was tried: Sand briquettes were allowed to harden 28

days and then were placed in a solution containing 250 grams of sulfuric acid (H_2SO_4) to the gallon. The solution was changed frequently and the briquettes broken at regular intervals. The disintegration of concrete by such acid water is shown by the following:

Age in the solution..	0 days	7 days	28 days	3 mos.	6 mos.	1 year
Tensile strength....	226	299	300	280	176	Disintegrated

Several years ago the question of the action of oil on concrete was brought up at one of the meetings of this society in connection with a paper by Prof. Carpenter. In his experiments oil was mixed in with the concrete. In the discussion which followed the reading of the paper, a number of gentlemen suggested that what was needed most was information relative to the action of oil on concrete which had already hardened, in view of the employment of concrete for machinery foundations, engine room and factory floors, etc., where it is subjected to the oil which leaks from the bearings of the machinery. I went home from this meeting and had a lot of sand briquettes made and allowed them to harden 2 weeks in air. These were stored in air, in engine oil, in cylinder oil, and in black oil. They were then broken at stated periods with the following results:

ACTION OF OIL ON CONCRETE					
Age in air.....	14 days				
Age in oil.....	7 days	28 days	3 mos.	6 mos.	1 year
TENSILE STRENGTH OF BRIQUETTES KEPT IN					
Engine oil.....	253	240	251	232	231
Cylinder oil.....	235	273	221	209	203
Black oil.....	234	222	181	131	Broke in clips
Air.....	248	233	287	303	293

It will be noted that the engine oil and the cylinder oil have practically no effect upon concrete. One would think that as the latter has a considerable proportion of animal oil in its composition it would be apt to effect appreciably concrete exposed to it. On the other hand, the action of the black oil seems strange in view of the fact that it is a straight mineral product. All of these briquettes had absorbed considerable oil, the actual gain in weight of each set at the end of the year being as follows:

	Per cent
Set in engine oil.....	10.6
Set in cylinder oil.....	10.0
Set in black oil.....	12.0

The briquettes in the black oil had not swollen perceptibly and seemed merely to be weak.

The experiments given above were all made upon very small test-pieces and hence the action of the solutions upon them were much more rapid than they would be upon a large mass of concrete, and while in most of the above cases a year was sufficient to completely disintegrate the test-pieces, in a large body of concrete, such as a pier or wall, many years at least would be required to bring about this result. The experiments merely serve to show that even very dilute solutions of the salts of magnesium and the sulfates in general do have a destructive action on concrete and that the generally proposed remedies do not appreciably retard this. They indicate the desirability of

employing low-alumina cements for sea-water construction. The experiments with the oils show that no destructive action is likely to take place where cement is used for floors in machine shops and engine rooms.

202 NORTH CALVERT ST.
BALTIMORE

THE DECOMPOSITION OF FELDSPAR AND ITS USE IN THE FIXATION OF ATMOSPHERIC NITROGEN

By WILLIAM H. ROSS¹

Received July 21, 1913

INTRODUCTION

The extensive search for sources of potash salts which has been undertaken in this country during the past two years has naturally led to renewed efforts in devising methods for its extraction from feldspar and other silicate rocks. The investigations in the use of feldspar as a source of potash have, however, not been confined to the past few years, but date back to the time when the part played by potash as a fertilizer in the production of crops was first recognized. Even as early as 1847 a British Patent, No. 11,555, was issued to Richard Albert Tilghman for a process of obtaining potassium sulfate from feldspar, by heating to bright redness for 8 hours, 2 parts of feldspar with 1 part each of limestone and gypsum. Within a few years a number of other patents appeared in England and other countries outlining methods for obtaining potash not only from feldspar, but also from leucite and other eruptive minerals.

The discovery of the importance of potash salts in agriculture took place also simultaneously with the discovery in 1851 of the great salt beds at Stassfurt, Germany, and in 1861 the first factory for refining crude potash minerals was established. The discovery at this time of such an enormous source of soluble potash salts naturally detracted from the interest which was being taken in the extraction of potash from the refractory silicates, and as a result no investigations for obtaining potash from these minerals were patented for 29 years.

The increasing demand in this country for potash fertilizers has again turned attention to the silicate rocks as a possible source. Owing to the commercial application of any successful method which might be devised, most of the investigations have been carried on in secret, and before the publication of any results, patents have been applied for in almost every case covering processes which have been proposed for the extraction of potash from this source. The number of patents of this kind which have been issued during the past few years is surprisingly large. No less than seven have been issued during 1912 alone, and it is known that a number of other patents have been applied for, but have not yet been issued, so that the processes to which they relate are still kept secret.

PROCESSES FOR THE DECOMPOSITION OF SILICATE ROCKS

The total number of patents which are concerned with the extraction of potash from silicate rocks num-

¹ Scientist in Soil Laboratory Investigations, Bureau of Soils, U. S. Dept. Agr.

ber at least 40. That so many patents should relate to processes all distinct from each other is not to be expected, and it is therefore not surprising to find that many have been issued which describe essentially the same process for the extraction of potash from insoluble silicates.

For convenience, these various processes may be considered in 3 groups as follows: (1) Processes which yield potash as the only product of value. (2) Processes which yield potash and some other salable material as a by-product. (3) Processes in which two or more operations are combined in one, yielding a fertilizer containing two or more of the essential plant foods—potash, phosphates and nitrogen in available form.

Of the 40 patents which have been referred to, about 50 per cent make no reference to any products of value which can be recovered other than the potash. From the results obtained in a previous publication¹ it is safe to conclude that processes of this kind cannot prove economical for the reason that the value of the product obtained, if based on the percentage of potash present, as is now universally done in the fertilizer industry, could not cover the cost of the raw materials, and the expense of operation.

The desirability of devising some method of treating feldspar which would produce at the same time some product of value in addition to the potash was early recognized, and about one-half of the patented processes referred to claim to have met this requirement. Among the various by-products which are considered possible of recovery in these processes may be mentioned alumina, silica, pigment, raw materials for the manufacture of glass, and hydraulic cement.

It has been shown² that when 1 part of feldspar and 3 parts of calcium carbonate are ignited to 1300–1400° the alkalis in the feldspar are completely volatilized and the residue has the composition required of Portland cement. Since the shale or clay used in the manufacture of cement contains small quantities of alkalis, it should follow that the percentage of alkalis in the dust which escapes from the kiln during the process of burning should be considerably greater than in the raw materials. This was found to be the case in most plants and in the case of several the concentration of the potash in the flue dust was very marked. In one plant examined the content of potash in the fine flue dust collected by the Cottrell precipitators, recently installed, amounts to as much as 40 per cent, mostly in the form of the oxide. Experiments are now being undertaken with a small cement mill to ascertain the practicability of recovering potash as a by-product in the manufacture of cement by the substitution of feldspar for clay or shale.

It has also been found³ that when 1 part of feldspar and 1.68 parts of lime are digested with water under pressure of about 17 atmospheres, upwards of 90 per cent of the potash in the feldspar passes into solution

in the form of the hydroxide. In this form the potash is worth per unit about 1.8 times the value it commands in the form of the chloride. The residue remaining insoluble has the composition required of Portland cement and would simply require ignition for its manufacture. The cost of the raw materials required for the process is estimated to be about \$6.70 per ton of feldspar, while the products obtained would have a value of about \$13.90, assuming for the feldspar an average potash content of 10 per cent.

The percentage of silica in feldspar is usually about double the combined percentages of potash and alumina present. When consideration is taken of the other reagents added in any treatment of the feldspar, it therefore follows that the insoluble residue remaining at the end of the process will amount to several times the quantity of potash, or potash and alumina present; consequently, in order that the residual material may find a market, when any considerable amount of potash is produced, it must be of such a nature that it can be used on a very large scale. Such may be said to be the case of the raw materials used in the manufacture of glass, of which upwards of one and a half million tons are required annually, but the process which produces cement as a product in the extraction of potash from feldspar has the advantage in that the quantity of cement used in this country is more than 10 times as great. Several of the patented processes of the second group which offer most promise are now being tested out on a comparatively large scale under the direction of the patentees. The results of these trials will determine conclusively the practicability of recovering potash from feldspar by these methods.

Some experiments have also been made in this laboratory on several of the remaining processes of this group, but the preliminary results obtained did not offer sufficient promise to justify continuing the work any further.

The first U. S. Patent (No. 16,111) dealing with the decomposition of feldspar was issued to Charles Bickell for a process which consisted in heating in a reverberatory or other suitable furnace to a light red heat for about 2 hours, 1 part feldspar, 0.5 part phosphate of lime, and 3 or 4 parts of air-slaked lime, all in a finely powdered condition. According to the patent, both the potash and the phosphate become available by this treatment. This process thus belongs to the third group into which processes for decomposing feldspar have been divided, and at first sight seemed to be particularly attractive, for if both the potash and phosphoric acid were rendered soluble as claimed by the patent, the method might be an economical one since, when used as a fertilizer, no separation of the constituents would be necessary and the mixture would be of value for its phosphoric acid as well as for its potash content.

It was found, however, that the calcium phosphate has a passive effect in this treatment of the feldspar and that no greater decomposition was produced in this way than when it was treated with calcium carbonate alone.

The process was further investigated by W. H.

¹ Bureau of Soils, U. S. Dept. Agr., *Circ.* 71.

² *Loc. cit.*

³ An article entitled "The Extraction of Potash from Silicate Rocks," giving a more detailed account of the results here referred to, is expected to be published shortly.

Waggaman of this laboratory who has shown in work soon to be published that when the ignition was made in an open vessel about 56 per cent of the potash was lost by volatilization, and of that which remained very little was water-soluble. None of the phosphoric acid was lost by volatilization under this treatment, but only 40 per cent was rendered citrate-soluble. A better result was obtained when there was added to the mixture about 0.2 part each of hematite and manganese dioxide for each part of feldspar, and the whole ignited to about 1400° for three-quarters of an hour. A limpid fusion resulted which, on cooling, was found to contain all of the potash and phosphoric acid in a citrate-soluble state, but neither was water-soluble.

FIXATION OF NITROGEN

The object of the present investigation was to test the efficiency of ignited feldspar in bringing about the fixation of nitrogen through the agency of the combined alumina or silica present, while there was the possibility that the potash would be set free at the same time. This would thus constitute a process which, like the foregoing, belongs to the third group.

Experiments in the fixation of nitrogen may be said to date back to the year 1785, when Cavendish first noted that an acid was formed when electric sparks were passed through a confined volume of air. The nature of the reaction, however, was at that time unknown. Fifteen years later Sir Humphry Davy observed the formation of nitric oxide when air was passed over platinum wire heated by an electric current. The function of the platinum in this reaction in acting as a catalytic agent was demonstrated by Gay-Lussac in 1864. Since then an immense amount of work has been done along this line. The popular literature on the subject is very extensive and a surprisingly large number of patents have been issued in Germany, Norway, United States, and other countries, on processes and equipment for fixing nitrogen by different methods.

The various processes recommended may be conveniently divided into four groups according as there is produced: (1) nitrates or nitrites; (2) ammonia; (3) nitrids; and (4) cyanids, or related compounds, as cyanamid.

Processes representative of all these groups have been or are being carried out on a large scale. The first and fourth have already developed into large industries. Extensive experiments are now being carried out in this and other countries on processes which relate to the third group, and there is a possibility that the fixation of nitrogen in the form of nitrids may ultimately prove more profitable than in any other way.

That certain metals, when heated, will combine with nitrogen to form nitrids has long been known. Lithium is the most marked in its action in this respect, and takes up nitrogen to form Li_3N even when exposed to moist air. When heat is applied in an atmosphere of nitrogen a violent reaction takes place. Magnesium ranks next to lithium in the tendency to combine with nitrogen. This property of magnesium

is made use of in the well-known method of removing nitrogen in the preparation of argon from the air. Among other metals which possess a marked affinity for nitrogen may be mentioned calcium, titanium, silicon and aluminum.

Instead of using the metal directly in the fixation of nitrogen, there may be used in preference a mixture of the oxide and carbon. In this way reduction of the oxide and fixation of nitrogen may be brought about in the same operation. The most noteworthy experiments in this direction have been made by Ottokar Serpek, who has worked out a technical process for fixing nitrogen on a large scale by igniting bauxite with carbon at $1800\text{--}2000^{\circ}$ in an atmosphere of nitrogen.¹ For this purpose a furnace was devised somewhat after the fashion of a rotary kiln having an electric furnace inserted in one section. The rotation of the kiln, while conveying the mixture to the electrical part of the furnace where the reaction takes place, acts also to bring the bauxite and carbon intimately together. The current of nitrogen under slightly increased pressure is passed through the kiln in an opposite direction to the mixed alumina and carbon. As the latter reaches the heated part of the furnace the reaction takes place, whereby there is formed aluminum nitrid (AlN) and carbon monoxide. It is supposed that the aluminum carbide which first has a tendency to form reacts with the alumina to form carbon monoxide and free aluminum which in the nascent state, at the temperature used, readily combines with nitrogen.

The compound thus formed is of a bluish gray color and on issuing from the furnace may contain upwards of 26 per cent of nitrogen. When boiled with alkaline hydroxide or sodium aluminate solution, or with water under pressure, the nitrogen present may be liberated as ammonia, while the aluminum is changed to hydroxide. This may be used over again, but at present the use of fresh bauxite seems to be more economical. In either case the material is rendered anhydrous before passing into the electrically heated kiln by calcining in a separate kiln with the carbon monoxide evolved from the reaction in the furnace kiln and which may be enriched with other combustible gases if necessary.

In some of his patents Serpek suggests that there should be added to the mixture of alumina and carbon about 5 per cent of some metal such as copper or iron which is capable of forming an alloy with aluminum. In other patents an increased yield of nitrid is reported to be brought about by mixing with the nitrogen about 0.1 per cent of some acid gas such as hydrochloric acid or sulfur dioxide. It is further stated that instead of using pure or impure alumina, such as natural bauxite, aluminum borates or silicates may be used for carrying out the process, but no results are given on the use of these minerals as in the case of bauxite.

Experiments along the same line as those outlined in Serpek's patents on the use of alumina for fixing

¹ U. S. Patents 867,615; 884,423; 888,044; 987,408; 996,032; 1,001,115; 1,016,526; 1,030,929; 1,040,439; 1,044,927; 1,044,928; 1,057,286; 1,060,500; 1,060,640.

nitrogen have been made by Tucker and Read.¹ The reactions were carried out in a stationary graphite electric resistance furnace. At temperatures below 1600° the yield of combined nitrogen was small, amounting to less than 3 per cent. The addition of hydrochloric acid gas or of sulfur dioxide to the nitrogen in the furnace gave lower results than when pure nitrogen was used, from which it was concluded that these gases are harmful rather than beneficial. The largest yield of nitrid, amounting to 22.7 per cent calculated as nitrogen, was obtained at a temperature between 1000° and 2000°.

EXPERIMENTAL RESULTS

In undertaking an investigation on the use of feldspar in fixing nitrogen a cylindrical gas furnace was used in the preliminary experiments. This was provided with holes in opposite sides through which was passed horizontally a glazed Royal Berlin porcelain tube 60 cm. long with an internal diameter of 2 cm. With this arrangement the portions of the tube inside the furnace could be repeatedly raised to 1200°, inside temperature, but as the temperature was increased to about 1400°, the tube soon became brittle and cracked. The tube was connected at one end with a hard glass combustion tube containing copper gauze over which, when heated to redness, the nitrogen was led under slightly increased pressure in order to remove the last traces of oxygen. The other end of the tube was closed with a stopper through which passed a glass tube that dipped into a flask containing water. This served as a trap to prevent any back flow of air and also indicated the rate of flow of nitrogen through the apparatus.

The nitrogen used in the experiments was prepared by dropping a strong sodium nitrite solution into a hot saturated ammonium chloride solution. The gas thus formed was stored in a gasometer and before using was dried by calcium chloride and sulfuric acid.

The feldspar used in the experiments was ground to pass a 100 mesh sieve and analyzed as follows:

SiO ₂	64.32%
Al ₂ O ₃	19.64
Fe ₂ O ₃	trace
CaO.....	0.16
MgO.....	0.08
K ₂ O.....	13.72
Na ₂ O.....	2.18
	100.10

This was mixed with sugar cane carbon in different proportions, wrapped in filter paper and inserted in the portion of the tube within the furnace, and then ignited in a current of nitrogen at temperatures up to about 1400°. The fixation obtained in any case was slight, amounting at most to about 1 per cent of the feldspar in the mixture.

Since, as already stated, the potash in feldspar may be set free by igniting with calcium carbonate, a number of experiments were made in which this compound was added to the mixture of feldspar and carbon. When this was done, not only was potash set free by volatilization from the feldspar, but the amount of nitro-

gen fixed at the same time was greatly increased. The porcelain tube in which the ignition was made extended for about 13 cm. outside the furnace, and this portion was therefore comparatively cool. The volatilized potash, however, was found to extend as a deposit not only along this length of the tube, but a portion even passed beyond the tube and was collected in the water trap through which the current was led; as the water contained a little phenolphthalein it acquired a deep pink color as the potash collected.

The percentage of the total potash in feldspar which is volatilized when the latter is ignited in an open vessel for an hour and a half at about 1400° with varying amounts of lime is given in the following table:

Proportion of feldspar to lime	Percentage of potash volatilized
5 to 3.....	6
5 to 4.....	16
5 to 5.....	27
5 to 6.....	61
5 to 7.....	83
5 to 8.....	95

When carbon, however, was added to the mixture of feldspar and calcium carbonate, or its equivalent of lime, and the ignition made in a current of nitrogen, instead of in an open vessel, the proportion of potash volatilized was found to be very greatly increased. Thus, when a mixture of 5 parts of feldspar, 5.4 parts of calcium carbonate, or 3 parts of lime, and 2.5 parts of carbon were ignited in nitrogen for one hour at 1200°, upwards of 50 per cent of the potash in the feldspar was volatilized, while at 1400° the loss of potash by volatilization was found to be complete. The amount of nitrogen fixed at the same time in this and other mixtures was kindly determined by Mr. T. C. Trescott of the Bureau of Chemistry, using the Kjeldahl method. The results given in the following table represent the mean of several determinations:

No. of expt.	Feldspar taken Grams	Carbon taken Grams	Calcium carbonate taken Grams	Temperature of ignition	Potash volatilized in percentage of total present	Nitrogen fixed in percentage of	
						Feldspar taken	Aluminum in feldspar
1.....	4	2	0.0	about 1200°	5.0	0.20	1.9
2.....	6	3	6.4	about 1200	0.83	8.0
3.....	4	2	4.3	about 1200	55.7	1.27	12.2
4.....	2	1	2.15	about 1200	1.44	13.8
5.....	4	4	4.3	about 1200	1.40	13.4
6.....	2	4	2.15	about 1200	38.0	1.45	13.9
7.....	4	2	2.15	about 1200	0.50	4.8
8.....	4	2	12.0	about 1200	78.0	0.44	4.2
9.....	4	2	0.0	about 1400	41.3	1.00	9.6
10.....	4	2	2.15	about 1400	98.0	1.68	16.1
11.....	4	2	4.3	about 1400	100.0	6.10	58.5
12.....	2	4	6.0	about 1400	100.0	5.21	50.6

It would seem from these results that varying the proportion of carbon between the limits given does not have much effect, under the conditions of the experiments, on the amount of nitrogen fixed. The minimum quantity of carbon taken was sufficient to combine with all the oxygen in the feldspar. Duplicate results, however, did not agree closely. This was no doubt due to the fact that it was not possible, with the arrangement in hand, to maintain a uniform tempera-

¹ *The American Fertilizer*, 37, No. 9, p. 39.

ture at all times and a comparatively small rise in temperature produced a considerable change in the amount of nitrogen fixed.

The calcium equivalent to the silica, as found by analysis, in 4 parts of the feldspar is equal to 4.3 parts of calcium carbonate. This proportion seems best suited in the fixing of nitrogen since smaller yields were obtained when the proportion of lime to feldspar was increased or decreased beyond this limit. The same results were obtained starting with the oxide of calcium as with the carbonate. Only a very slight amount of nitrogen was fixed when a mixture of lime and carbon were ignited at 1400° in the absence of feldspar.

The increase of fixation with time of ignition is shown in the following table, when 4 parts of feldspar, 2 parts of carbon and 4.3 parts of calcium carbonate were ignited for different lengths of time.

Time of ignition Hours	Temperature	Potash volytilized in percentage of total present	Nitrogen fixed in percentage of	
			feldspar taken	aluminum in feldspar
1.....	about 1200°	55.7	1.27	12.2
2.....	about 1200°	68.9	1.34	12.9
4.....	about 1200°	83.0	1.68	16.1
1.....	about 1400°	100.0	6.10	58.5
2.....	about 1400°	100.0	7.44	71.5

Since the nitrogen in aluminum nitrid amounts to 51.6 per cent of the aluminum, it follows that the nitrogen fixed in the last two experiments is greater than what would correspond to the aluminum in the feldspar. No direct experiments have yet been made to determine in what form the nitrogen is combined, whether as nitrid or carbo-nitrid of silicon or aluminum. When boiled with water the material gave off ammonia very slowly, and even slowly when boiled with sodium hydroxide solution although in this case the ammonia was evolved more rapidly than when the digestion was made with water alone.

Equipment is now being installed to carry on the experiments on a larger scale and at higher temperatures. In the meantime it was thought advisable to publish the preliminary results obtained.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

THE LEACHING OF POTASH FROM FRESHLY CUT KELP

By A. R. MERZ¹ AND J. R. LINDEMUTH²

Received June 27, 1913

Drift kelp usually has a very low content of potash

or rather potassium chloride. It has been currently reported that the loss of potassium chloride from the freshly cut plant proceeds quite rapidly. Theoretically, there should be a distribution of the base between the plant and the water in which it lies, and this redistribution might reasonably be expected to commence at once, and even to be much augmented or accelerated because of the relatively high content of sodium chloride in sea water. This problem is one of considerable economic importance, since it has been proposed in the harvesting of kelp as a raw material for the production of potassium salts, to tow the cut kelp from the groves to the landing and thus avoid lifting the material upon a barge or boat.

In order to obtain some information and data bearing directly on this economic question, Professor W. C. Crandall, of the Scripps Biological Station, at La Jolla, California, collected two large samples of *Macrocystis* on a recent cruise of the yacht, "Agazzi", of that station, towing these samples and taking subsamples from time to time which were forwarded to the laboratory of the Bureau of Soils, in Washington, for analysis. One of the large samples for the leaching experiment was collected near Pt. Loma and the other near Coronado Island. The subsamples, on their receipt in Washington, had commenced to ferment. This fact, however, could not have any particular influence on the data here given. The tables which follow are self-explanatory. The analytical methods employed have been described in THIS JOURNAL, 4, 431 by Turrentine, and acknowledgment is here made to Mr. T. C. Trescott, of the Bureau of Chemistry, who kindly made the nitrogen determinations for us.

From this examination it is evidently a matter of considerable difficulty to obtain a fair average sample of wet kelp. It also appears that freshly cut kelp, when immersed in sea water, does not, at least at first, lose its potash content very rapidly.

Attention is called to the analysis of "sea lettuce" in Table II. This is not a kelp but a rock weed rather common on the Pacific coast. Algae other than the giant kelps have not usually shown a high potash content, but this analysis indicates that the matter is worthy of further investigation. The difficulties to be apprehended in harvesting rock weeds, however, do not leave much promise for their economic importance at present, even though they should be found to have a high content of potash or other valuable

TABLE I—SAMPLE TAKEN NEAR CORONADO ISLANDS

No.	Time exposed	Per cent K ₂ O	Per cent sol. salts	Per cent org. matter	Per cent ash	Per cent KCl	Per cent N	Per cent I	Remarks
1m.....	None } fresh cut	12.48	31.46	65.38	3.16	19.72	0.98	0.16	Dried and sent by mail
1ex.....	None }	13.47	31.26	65.98	2.76	21.28	0.79	0.14	Wet, sent by express in jar
1A.....	3 hrs.	15.56	34.00	62.38	3.62	24.59	0.95	0.13	Wet, sent by express in jar
1B.....	6 hrs.	17.30	38.26	58.66	3.08	27.33	1.00	0.13	Wet, sent by express in jar
1C.....	14 hrs.	17.64	38.30	58.30	3.40	27.87	1.07	0.06	Wet, sent by express in jar
1D.....	17 hrs.	13.35	31.96	54.96	3.08	21.10	0.83	0.10	Wet, sent by express in jar
1E.....	20 hrs.	10.74	26.36	70.66	2.98	16.97	0.90	0.13	Wet, sent by express in jar
1F.....	None }	18.28	36.78	60.86	2.36	28.89	0.51	0.13	Stems only, dried and sent by mail
1G.....	None } fresh cut	9.90	25.94	70.18	3.88	15.64	0.84	0.07	Leaves only, dried and sent by mail

¹ Scientist in Soil Laboratory Investigations, Bureau of Soils, U. S. Dept. Agr.

² Scientist in Fertilizer Investigations, Bur. of Soils, U. S. Dept. Agr.

constituent, and the importance of the matter probably lies in showing that their occasional or accidental

TABLE II—SAMPLER FROM NEAR PT. LOMA

No.	Time exposed	Per cent K ₂ O	Per cent sol salt	Per cent org. matter	Per cent ash	Per cent KCl	Per cent N	Per cent I	Remarks
2A.....	None	15.82	40.88	47.32	11.80	25.00	2.77	0.18	Wet, sent in jar
2B.....	3 1/2 hrs.	13.43	34.82	56.54	8.64	21.22	2.66	0.19	Wet, sent in jar
2C.....	15 1/2 hrs.	14.96	37.66	52.76	9.58	23.64	2.40	0.15	Wet, sent in jar
2D.....	18 1/2 hrs.	13.05	34.34	60.12	5.54	20.62	1.77	0.15	Wet, sent in jar
2E.....	21 1/2 hrs.	11.00	30.22	62.52	7.26	17.38	1.85	0.16	Wet, sent in jar
2F.....	24 1/2 hrs.	11.59	30.52	59.92	9.56	18.31	2.10	0.14	Wet, sent in jar
2G.....	27 1/2 hrs.	13.68	38.94	50.56	10.50	21.62	2.22	0.24	Wet, sent in jar
2H.....	30 1/2 hrs.	10.31	27.84	62.38	9.78	16.29	1.97	0.14	Wet, sent in jar
2I.....	42 1/2 hrs.	16.39	38.78	53.30	7.92	25.90	2.22	0.21	Wet, sent in jar
2J.....	45 1/2 hrs.	11.77	32.44	60.54	7.02	18.60	1.99	0.22	Wet, sent in jar
2K.....	48 1/2 hrs.	16.69	39.72	54.22	5.96	26.37	1.79	0.19	Wet, sent in jar
2L.....	51 1/2 hrs.	15.77	40.80	45.88	13.32	24.92	2.29	0.22	Wet, sent in jar
2M.....	63 1/2 hrs.	16.74	42.58	45.36	12.06	26.45	2.49	0.21	Wet, sent in jar
2N.....	66 1/2 hrs.	16.75	38.64	55.28	6.08	26.46	1.91	0.19	Wet, sent in jar
2O.....	72 1/2 hrs.	14.67	35.58	58.12	6.30	23.18	1.88	0.19	Wet, sent in jar
2P.....	75 1/2 hrs.	12.61	34.74	55.46	9.80	19.93	2.66	0.22	Wet, sent in jar
2Q.....	87 1/2 hrs.	15.54	40.84	48.92	10.24	24.56	2.47	0.19	Wet, sent in jar
2R.....	90 1/2 hrs.	17.62	41.42	49.48	9.10	27.84	2.16	0.16	Wet, sent in jar
2S.....	93 1/2 hrs.	17.03	42.44	44.50	13.06	26.90	2.28	0.20	Wet, sent in jar
2T.....	96 1/2 hrs.	15.61	37.80	54.42	7.78	24.67	2.16	0.10	Wet, sent in jar
2U.....	99 1/2 hrs.	20.28	46.28	43.96	9.76	32.05	2.12	0.20	Wet, sent in jar
2V.....	111 1/2 hrs.	15.72	38.80	51.44	9.76	24.84	2.26	0.23	Wet, sent in jar
2W.....	135 1/2 hrs.	15.60	39.24	48.74	12.02	24.65	2.57	0.27	Wet, sent in jar
2.....	111 1/2 hrs.	15.27	34.52	57.42	8.06	24.13	1.80	0.18	Dried and sent by mail
M. P.....		30.00	57.10	32.76	10.14	47.41	1.66	0.06	Sea lettuce from Marrowstone Point

presence in harvested kelp is not detrimental to the value of the kelp.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

A POSSIBLE COMMERCIAL UTILIZATION OF NELSONITE

By WILLIAM H. WAGGAMAN¹

Received June 23, 1913

INTRODUCTION

In Nelson County, Va., there are large bodies of rock locally known as Nelsonite which consist essentially of the two minerals ilmenite and apatite. The material is not only of scientific interest but in the light of some recent experiments performed in this laboratory may be of considerable commercial importance.

The rock occurs in the foothills of the Blue Ridge near Roseland, Va., about 7 miles northwest of Arrington, a station on the Southern R. R., and 24 miles northeast of Lynchburg. According to Watson² it is probably of pre-Cambrian age and occurs in dikes which are in places over 65 feet thick and 2,100 feet in length as exposed on the surface. The formation can be traced in a general northeast southwest direction for about 7 miles. Watson described it as "a hard rock composed of granular white apatite and black ilmenite." After weathering, however, the rock can be readily disintegrated and a more or less clean separation made of the two minerals by either of the methods described further on in this paper.

ILMENITE

Ilmenite or titanite iron is a black crystalline mineral having feebly magnetic properties. It has a specific gravity when pure of 4.5 to 5.0 and the following formula and composition:

FeTiO ₃	Titanium oxide (TiO ₂).....	52.7 per cent
	Iron protoxide (FeO).....	47.3 per cent

According to Dana,³ however, the ratio of iron to

¹ Scientist in Fertilizer Investigations, Bureau of Soils, U. S. Dept. Agr.

² "Mineral Resources of Virginia," 1907, p. 300; "Economic Geology,"

U. S. Geol. Survey, 1909, pp. 206-7.

³ "A System of Mineralogy," 1892, pp. 217-219.

titanium varies widely corresponding to the general formula $MFeTiO_3.NFe_2O_3$.

Ilmenite is rather widely distributed in nature, occurring in beds in gneiss and other crystalline rocks; also in small particles in many crystalline rocks and frequently associated with magnetite. It is used in the manufacture of ferro-titanium for the steel industry. In 1911 there were 51.17 tons of ferro-titanium imported into this country valued at \$22,700, which gives an average price of \$443.61 per ton.

APATITE

Apatite or phosphate rock is a brittle crystalline mineral which varies in color from almost white to dark green-red and brown. There are two main varieties of this mineral; namely, chlor-apatite and fluor-apatite, the latter being much more plentiful than the former. The specific gravity of apatite varies from 3.17 to 3.23 and the formula and composition of the two varieties according to Dana, are as follows:

Chlor-apatite, $CaCl.Ca_4(PO_4)_3$ =	P_2O_5 = 41.0 per cent
	CaO = 53.8 per cent
	Cl = 6.8 per cent
Fluor-apatite, $CaF.Ca_4(PO_4)_3$ =	P_2O_5 = 42.3 per cent
	CaO = 55.5 per cent
	F = 3.8 per cent

Apatite, however, is seldom found absolutely pure and though widely distributed in nature does not often occur in minable quantities. On treatment with sulfuric acid it yields a very high-grade superphosphate, and if it were not for the fact that the better deposits are rather inaccessible and that careful picking or "cobbing" is necessary before a product sufficiently high-grade for the market is obtained, this mineral would be more extensively used in the fertilizer industry.

SEPARATION OF APATITE AND ILMENITE

At first sight the association of apatite and ilmenite in a rock would seem to seriously affect the commercial value of both of these minerals. In the manufacture

of steel, phosphorus is the most dreaded impurity which can occur in the iron or iron ore used, so that ilmenite containing over 1 or 2 per cent of this element would be rejected as dangerous.

On the other hand, the presence of comparatively small percentages of iron in phosphate rock nearly always causes trouble in the acid phosphate produced therefrom, and when this element is present in large amounts it often renders the acid phosphate unfit for use.

According to Watson¹ the ratio of apatite to ilmenite in nelsonite varies widely from rock consisting largely of the former mineral to that in which ilmenite predominates. Before such a deposit can be economically worked, therefore, it seems essential that a method be devised for making a clean separation of the two minerals.

There are two methods which suggest themselves for effecting such a separation. The first is based on the difference in the specific gravities of the minerals, and the second on the magnetic properties of the ilmenite. The ratio of the specific gravity of apatite and ilmenite is as 3.2 to 4.5. This difference is sufficiently great to warrant a fairly clean separation provided the rock is crushed to uniform size. Unless it is ground very fine, however, a preliminary screening is necessary before suspending the material in water. The various modifications of the methods of separating substances by the difference in their specific gravities are well known and need not be enumerated here.

A separation of the two minerals by means of a magnetic separator has also proved feasible but owing to the rather feeble magnetic properties of the ilmenite it is not entirely removed from the apatite, by this method, and though a preliminary heating enhances somewhat this magnetism, such a procedure would probably prove too expensive in commercial practice.

From a number of experiments with nelsonite it has been pretty well demonstrated that while ilmenite can be fairly easily removed from apatite by either of the methods outlined above it is practically impossible to effect a clean separation by mechanical means, since the nature of the rock is such that there will always be particles of the two minerals which adhere strongly to each other.

We must, therefore, resort to chemical means to bring about this desired end. In the experiments described below it is shown that ilmenite may be almost completely freed from apatite by means of sulfuric acid, with a minimum amount of waste and without involving any great expense. Moreover, all of the products obtained during the process can be utilized commercially.

EXAMINATION AND SEPARATION OF THE MINERALS IN NELSONITE

A typical sample of the rock was submitted to a microscopic examination by Mr. W. H. Fry of this Bureau and found to consist essentially of crystallized ilmenite and partially decomposed apatite. The material was then crushed to pass a $\frac{1}{2}$ mm.

sieve and a separation made by means of a strong magnet. Owing to the rather feeble magnetic qualities of part of the ilmenite this separation was made at the expense of the apatite which was afterwards found to contain a considerable amount of the former mineral in a finely divided state.

The results of this separation are given below:

	Per cent
Nelsonite as separated by magnet in the laboratory contained.....	
Apatite.....	23.8
Ilmenite.....	76.2

Both the ilmenite and apatite thus separated were analyzed by Mr. C. F. Miller of this Bureau, with the following results:

	Per cent
Ilmenite as separated by magnet in the laboratory contained.....	
FeO.....	44.2
TiO ₂	44.5
P ₂ O ₅	0.8
Apatite as separated by magnet in this laboratory contained.....	
FeO.....	6.5
P ₂ O ₅	33.3
Ca ₃ (PO ₄) ₂	72.8

Although the amount of phosphoric acid remaining in the separated ilmenite was less than 1 per cent, such a clean separation could hardly be attained in actual works practice. Even this amount of phosphoric acid is objectionable and would probably seriously affect the sale of the material.

Preliminary experiments showed that ilmenite is almost entirely unattacked by dilute sulfuric acid, while it is well known that apatite is acted upon quite energetically by the same acid: so 3 samples of the separated ilmenite of 10 grams each were treated with sulfuric acid of different strengths. The mixtures were warmed slightly and stirred intermittently for 20 minutes. At the end of that time the acid was diluted with water, filtered and washed. The filtrate was made up to 200 cc. and the percentages of iron and phosphoric acid thus dissolved determined in the two solutions. The residual ilmenite was again weighed and also analyzed for phosphoric acid.

The results of these analyses are given in Tables I and II.

TABLE I—ANALYSIS OF SULFURIC ACID EXTRACTS OF ILMENITE

3 samples of 10 grams each treated with 50 cc. of sulfuric acid of various strengths.

Strength of H ₂ SO ₄ used	Amount of P ₂ O ₅ extracted by acid Per cent	Amount of Fe ₂ O ₃ extracted Per cent
50° B.	0.22	0.19
32° B.	0.46	0.29
25° B.	0.41	0.32

TABLE II—ANALYSIS OF ILMENITE AFTER EXTRACTION WITH SULFURIC ACID

Strength of acid used in extraction	Loss in weight of ilmenite Per cent	Amount of P ₂ O ₅ remaining in ilmenite Per cent
50° B.	1.04	0.47
32° B.	1.75	0.31
25° B.	1.58	0.36

From the data given in Tables I and II it will be seen that the apatite remaining in ilmenite after the mechanical separation can nearly all be extracted by means of dilute sulfuric acid (32° B.) without appreciably affecting the ilmenite. The amount of iron

¹ "Mineral Resources of Virginia," 1907.

thus dissolved is too small to lower the value of the acid extract which can be used in treating the separated apatite to produce superphosphate.

While this acid extract is considerably weaker than that employed in the manufacture of acid phosphate it could be readily brought to the desired concentration, either by evaporation, or by mixing it with the sulfuric acid which is shipped in tank cars; this latter acid has a strength of 60° B.

The apatite as separated in the laboratory contained a considerable amount of iron, but this impurity should cause no trouble in the making of superphosphate since only the compounds of this element which are soluble in sulfuric acid cause the objectionable reversion to take place or render the acid phosphate too sticky for use.

ECONOMIC CONSIDERATIONS

If both the ilmenite and apatite can be disposed of at a fair price the mining of nelsonite should prove quite profitable. Unfortunately the market for ilmenite is rather limited at present, and it is doubtful whether the steel industry would handle the large tonnage which extensive development could produce. If nelsonite could be depended upon to yield an average of 50 per cent of apatite the exploitation of the rock for this mineral alone would be well worth while, but it is doubtful if the general mine run contains such a high percentage of apatite.

The production of apatite from nelsonite would undoubtedly be more expensive than the mining and preparation of Florida phosphate, since the rock is quite hard and would require rather fine grinding before a separation could be made. On the other hand, the average content of phosphate rock in nelsonite is considerably higher than it is in the Florida deposits. The amount of phosphate rock actually marketed from this latter state is probably not more than 15 per cent of the total material taken from the mines; in other words, every ton of phosphate produced involves the handling of over 6 tons of waste material.

The following figures, while approximate, are conservative and give some idea of the cost of mining and separating the two minerals in nelsonite:

TABLE III—COST OF MINING NELSONITE AND MAKING A MECHANICAL SEPARATION OF THE TWO MINERALS, APATITE AND ILMENITE PER TON

Cost of mining.....	\$1.00
Cost of grinding.....	0.50
Cost of mechanical separation.....	0.25
Total cost.....	\$1.75

Assuming that 1 ton of nelsonite will yield $\frac{1}{2}$ ton each of ilmenite and apatite then the cost of preparing this amount of ilmenite for the market will be as follows:

TABLE IV—COST OF PREPARING ONE-HALF TON OF ILMENITE FOR THE MARKET

$\frac{1}{2}$ expense of mining and separating minerals.....	\$0.88
$\frac{1}{2}$ ton of sulfuric acid (60° B.) at \$8.00 per ton.....	4.00
Cost of washing ilmenite ($\frac{1}{2}$ ton).....	0.30
Cost of drying ilmenite ($\frac{1}{2}$ ton).....	0.15
Total cost of $\frac{1}{2}$ ton ilmenite.....	\$5.33

The sulfuric acid extract after concentration can

be used in making acid phosphate by mixing it with an equal weight of the separated apatite.

The cost of manufacturing this product would be approximately as follows:

TABLE V—COST OF MAKING ONE TON OF ACID PHOSPHATE FROM ONE HALF TON OF APATITE SEPARATED FROM NELSONITE

$\frac{1}{2}$ expense of mining and separating minerals.....	\$0.88
$\frac{1}{2}$ ton of sulfuric acid (60° B.) (cost included in expenses for cleaning ilmenite).....	4.00
Cost of drying apatite ($\frac{1}{2}$ ton).....	0.15
Cost of mixing and handling.....	0.50
Total cost of 1 ton acid phosphate.....	\$1.53

The total cost of mining 1 ton of nelsonite (having the above composition) and producing therefrom $\frac{1}{2}$ ton of ilmenite (practically free from phosphorus), and 1 ton of acid phosphate (16 per cent P_2O_5) would be (exclusive of interest on investment, insurance and taxes) about \$6.86 per ton—an amount which would be more than covered by the value of the acid phosphate produced.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

QUANTITATIVE DETERMINATION OF ROSIN IN PAPER

By C. FRANK SAMMET

Received July 7, 1913

As the necessity for securing record papers so free from chemicals and deleterious substances that they may be preserved indefinitely becomes more apparent, the importance of the determination of the sizing materials in the papers, particularly rosin, increases. Obviously, the resistance of the cellulose fibers to the action of light, heat, moisture and fumes is greatest in paper free from harmful materials. In carefully prepared specifications for durable papers it is customary to limit the percentage of rosin which may be present, as this substance, especially when used in large quantities, materially hastens discoloration and deterioration. Limits for rosin are now included in government paper specifications.

ALCOHOL METHODS

Of the numerous methods used for estimating the amount of rosin in paper, many are based on its extraction with alcohol, modifications being introduced in the subsequent treatment of the solution containing the extracted rosin.

Turbidity Method.—The turbidity produced by the precipitation of rosin from solution, on diluting the alcoholic extract with water, is compared with the turbidity produced in a like manner in an alcoholic solution, the rosin concentration of which is known. Although in many cases 0.0002 gram differences in the same solution may thus be detected, it was found that in some papers the determinations varied 25 or even 50 per cent from the actual amount of rosin present. Since more than 0.006 gram of rosin precipitated in 100 cc. of water interferes with the delicacy of the comparison, the quantities used must be so small that the percentage error is greatly affected by the uniformity of precipitation, which depends upon such factors as the sequence of operation, time allowed for precipitation and subsequent comparison,

the amount of alcohol present, the foreign materials extracted by alcohol, and the undetermined factors influencing the size of the precipitated rosin particles. It is probable, however, that if the alcoholic extract were freed from foreign materials by evaporation, extraction with ether, and washing with water, as described below, the turbidity method would give more accurate results.

Acidified Alcohol Method.—The rosin is precipitated from the alcoholic extract by dilution with acidulated water, filtered off, washed, dried, and weighed. The sources of error here are incomplete precipitation in the presence of colloidal materials, the escape of minute suspended particles through the filter, and the contamination of the rosin by the co-precipitation of foreign materials.

Direct Evaporation Method.—The acidulated alcoholic solution with which the rosin is extracted is evaporated directly and the residue weighed. This method gives results which, in some instances, may be too high by 60 per cent, because of the contamination by such foreign substances as glue, invert starch, cellulose, soda, aluminum salts, fats and greases, which are also removed from the paper by the acidified alcohol.

Schumann's Method.¹—The rosin, having been extracted by a dilute solution of alkali, is precipitated from the extract, filtered off, washed, dried, and weighed. The difficulty of removing the alkali resinate, especially from soft papers which are easily pulped by the action of the alkali, and the contamination of the precipitated rosin by foreign substances extracted by the alkali renders this method unsatisfactory. Were this precipitate of rosin taken up in ether and the ether extract washed with water, then evaporated and weighed, more accurate results could be obtained, although the loss from incomplete extraction and washing would still occur.

ACIDIFIED ETHER METHOD

Acidified ether is the solvent in this method, the ether extract of the paper being directly evaporated, dried, cooled and weighed. It is open to the objection that the resinsates are not readily extracted by ether.

ALCOHOL-ETHER METHOD

Because of the objections to the current methods, a procedure reasonably accurate and at the same time simple in execution was sought. The modifications of the method as first devised,² which have been developed by experience, are incorporated in the following procedure:

Cut 5 grams of paper into strips approximately one-half inch wide and fold them in numerous small crosswise folds. Place the folded strips in a Soxhlet extractor and fill with acidulated alcohol diluted to approximately 83 per cent, made by adding to 100 cc. of 95 per cent alcohol 15 cc. of acidulated water containing 5 cc. of glacial acetic acid to 100 cc. of distilled water. Place the Soxhlet flask directly in the boiling water of a steam bath and extract by siphoning from six to twelve times, according to the nature of

the paper. Wash the alcoholic extract of rosin, which may contain foreign materials, into a beaker and evaporate to a few cubic centimeters on a steam bath. Cool, take up in about 25 cc. of ether, transfer to a 300 cc. separatory funnel containing about 150 cc. of distilled water to which has been added a small quantity of sodium chloride to prevent emulsion, shake thoroughly, and allow to separate. Draw off the water into a second separatory funnel and repeat the treatment with a fresh 25 cc. portion of ether. Combine the ether extracts which contain the rosin and any other ether-soluble materials and wash twice, or until the ether layer is perfectly clear and the line between the ether and water is sharp and distinct, with 100 cc. portions of distilled water to remove salts and foreign matter. (Should glue, which is extracted from the paper by alcohol, interfere by emulsifying with the ether, it may be readily removed by adding a strong solution of sodium chloride to the combined ether extracts, shaking thoroughly and drawing it off, repeating if necessary, before washing with distilled water.) Transfer the washed ether extract to a weighed platinum dish, evaporate to dryness and dry in a water oven at from 98° to 100° C. for exactly one hour, cool, and weigh. This length of time is sufficient to insure complete drying; prolonged heating causes a continual loss of rosin.

It may be noted that any alcohol- and ether-soluble fats, waxes or other foreign materials present in the paper will be extracted with the rosin. These substances, however, if present at all, occur in such small amounts in high-grade papers that their influence on the result is negligible. It has been found that the quantity of rosin obtained from 5 grams of paper is sufficient for accurate work, and that a greater amount of paper materially interferes with complete extraction within a reasonable time. The folding of the strips is important, as it prevents the sticking together of the pieces when wet and consequent incomplete extraction which results when the paper is merely torn or cut into small pieces. It is well, although not essential, to saturate the folded strips with acidulated alcohol when they are placed in the Soxhlet flask, as this hastens the breaking up of the resinsates.

If the alcohol is too dilute, the extraction of rosin from the paper is incomplete, and large quantities of glue interfere with the subsequent separation with ether. If acidulated alcohol of 95 per cent concentration is used, the acid does not break up the resinsates which, therefore, will not be extracted. By placing the Soxhlet flask directly in the boiling water of a steam bath, distillation is hastened and the solvent in the extraction chamber is kept hot by the surrounding steam, which completes the extraction in a minimum length of time.

It was found that neutral 95 per cent alcohol does not completely remove the rosin within a reasonable time, probably because resinsates are not readily soluble. A representative instance occurred when 10 grams of paper were extracted in a Soxhlet flask with 125 cc. portions of 95 per cent neutral alcohol by the alcohol-ether method, the following results being obtained:

¹ Sindall, "Elementary Manual Paper Technology," 1910.

² U. S. Dept. Agr., Office of the Secretary, Report 89, 1909.

TABLE I—ROSIN OBTAINED FROM NEUTRAL ALCOHOL SOLUTION

No. of extraction	Time of extraction Hours	Rosin obtained Per cent
1	4	1.786
2	3	0.138
3	3	0.094
4	3	0.066
5	4	0.040

It was also found that the percentage removed in successive extractions with neutral 95 per cent alcohol varies with the amount of rosin originally present and with the nature of the paper extracted.

The alcohol-ether method has been subjected to tests, which may best be illustrated by the following typical examples taken from numerous determinations:

Ten grams of rosin were dissolved in a solution of sodium carbonate and made up to 1000 cc. Twenty-five cubic centimeters, representing 0.25 gram of rosin, were withdrawn from this solution, the rosin precipitated by the addition of aluminum sulfate and acetic acid, and the whole then extracted with two 25 cc. portions of ether. The ether extract was washed with distilled water, as directed in the method, evaporated, dried at 100° C. for one hour, cooled, and weighed. The dried material weighed 0.2509 gram, agreeing closely with the amount of rosin taken.

The method was further tested by extracting many different kinds of paper and determining the amount of rosin present. A second extraction was made on the same sample of paper and the rosin then taken up in ether and determined, with the results shown in Table II. Third and fourth extractions with 83 per cent alcohol have not given, in any case, more than 0.04 per cent of rosin.

TABLE II—DETERMINATION OF ROSIN

Kind of paper	Amount of rosin extracted	
	First extraction Per cent	Second extraction Per cent
Ledger.....	1.72	0.02
Bond.....	1.90	0.01
Writing.....	1.20	0.06
Sized and supercalendered printing.....	0.81	0.04
Manila.....	1.48	0.03
Double coated.....	1.57	0.05

The effect of the concentration of acidified alcohol on the extraction of rosin is shown in the following table. Ninety-five per cent alcohol diluted to the approximate percentage given was used in the determination:

TABLE III

Extraction No.	Amount of rosin extracted			
	86 per cent alcohol	83 per cent alcohol	79 per cent alcohol	73 per cent alcohol
Ledger paper:				
1.....	1.67	1.70	1.63	1.53
2.....	0.02	0.02	0.03	0.09
3.....	0.01	0.01	0.02	0.01
Total.....	1.70	1.73	1.68	1.63
Writing paper:				
1.....	2.17	2.03	1.96	2.00
2.....	0.07	..	0.06	0.12
3.....	0.01	0.03	0.03	0.09
Total.....	2.25	2.06	2.05	2.21

These results show that a concentration of 86 or

83 per cent is preferable to one of 79 or 73 per cent, which gives slightly lower results. Even at these latter concentrations, however, the results are within the experimental error of 0.20 per cent, except in the case of the 73 per cent concentration in the first extraction of the writing paper where the percentage error is 0.21.

The variations in results due to sampling are shown by the following figures, obtained by extracting different sheets of the same sample of ledger paper as that reported in Table III.

TABLE IV

Extraction No.	Amount of rosin extracted			
	86 per cent alcohol	83 per cent alcohol	79 per cent alcohol	73 per cent alcohol
Sample I:				
1.....	1.66	1.67	1.56	1.65
2.....	0.09	0.02	0.07	0.04
3.....	0.01	0.01	0.04	0.08
Total.....	1.76	1.70	1.67	1.77
Sample II:				
1.....	1.79	1.79	1.70	1.75
2.....	0.04	0.04	0.02	0.02
3.....	0.02	0.04	0.03	0.03
Total.....	1.85	1.87	1.75	1.80

These results are entirely within the experimental error of 0.20 per cent, as far as the 86 and 83 per cent concentrations are concerned.

A comparison of the results obtained by the alcohol-ether method with the results obtained by the alcohol evaporation and acidified ether methods, in which the total extract is dried, weighed and calculated as rosin in each case, gave the following results:

TABLE V

Method:	Amount of rosin extracted						
	Machine finished printing Per cent.	Writing Per cent.	Ledger (rag) Per cent	Coated. Per cent	Ledger (wood) Per cent	Bond (wood) Per cent	Wrapping (wood) Per cent
Acidified alcohol direct evaporation.....	2.87	1.39	1.85	30.6	2.61	2.82	1.79
Acidified ether direct evaporation.....	2.65	1.22	0.94	2.86	1.66	1.90	1.20
Acidified alcohol-ether....	2.47	1.18	1.70	0.92	1.25	2.00	1.22

This table shows that the acidified alcohol extract followed by direct evaporation gives results which are too high, due to the presence in the extract of both soluble and insoluble foreign material. In the alcohol-ether method these materials are eliminated through precipitation and washing.

Acidified ether does not extract as much rosin in the same number of siphonings as acidified alcohol. The method has a tendency to yield low results. In some instances, however, insoluble material is separated from the paper, thereby giving results which are too high.

The amount of material which may be extracted from coated paper by acidified alcohol is indicated when the extract is evaporated directly. To report such material as rosin is obviously erroneous. The acidified alcoholic extract was very opalescent and gave positive tests for glue and casein. Ordinarily,

of course, one would not report such results as rosin. In those cases, however, where the error is less obvious the analyst may frequently fail to detect it.

CONCLUSIONS

The alcohol-ether method has consistently given the most accurate and concordant results in this laboratory in all comparative work. Contrary to our first experience with it, when an insufficient amount of acid was used, extraction with one portion of acidified alcohol, making from six to twelve siphonings, has been found to be sufficient for all practical purposes. The results, when 83 per cent alcohol is used, are within the experimental error of 0.20 per cent, as are the variations due to sampling. No other procedure tried has proved equally satisfactory.

LEATHER AND PAPER LABORATORY
BUREAU OF CHEMISTRY
WASHINGTON

COLORIMETRIC METHOD FOR TITANIUM IN IRON AND STEEL

By C. R. McCABE
Received March 6, 1913

In the colorimetric method for titanium, the color is usually produced in a sulfuric acid solution of the iron or steel. The color of the ferric sulfate is in most cases much more intense than that of the titanium. The color employed for comparison is therefore a blend of two colors in which the color on which we base our method is the subordinate one. If the quantities of iron present in standard and test are the same, it follows that so far as iron is concerned the two solutions have the same color at equal volumes. If comparison be attempted at unequal volumes, even though the divergence be slight, the more concentrated solution contains a more intense iron color than the other. Hence, we must have a standard which contains the same percentage of titanium as the test sample, within very narrow limits.

This consideration led the writer to seek some plan whereby a standard would be always available precisely like the test sample. The plan adopted is to produce the color in a sulfuric acid solution of the iron or steel and then imitate it in a solution of a non-titanium steel by adding a standard solution of titanium from a burette.

PREPARATION OF TITANIUM STANDARD SOLUTION

Place about 100 grams of ferro-titanium in a dish and pour over it about 50 cc. of strong HCl. Heat, and when the solvent action has progressed for a few moments add 5 cc. of nitric acid (sp. gr. 1.2). Continue heating until the acid is about half evaporated, dilute with 15 or 20 cc. water and filter through a large filter paper. Treat the ferro-titanium again with hydrochloric and nitric acids, dilute, and filter in this manner a dozen times or more until the desired quantity of ferro-titanium has been dissolved. Simultaneously with the solution of the ferro-titanium the combined filtrates are evaporated in a large beaker on a hot plate. Evaporate until separation of titanic acid is observed. Pour into several separatory funnels, and add to each 50 cc. ether. Make repeated

ether extractions of the iron until the titanic acid is free of iron as shown by the potassium sulfocyanide test. Combine the several acid solutions and place in a 400 cc. beaker. To the titanic acid emulsion add 150 cc. sulfuric acid (1 : 3). Heat and filter from the insoluble portion, which is usually slight. Dilute the filtrate to about 700 cc., in a liter beaker, add ammonia in excess, boil and allow the precipitate to settle. Decant or siphon away the supernatant solution and wash the hydrated titanic acid free of chlorides by decantation.

Dissolve the titanic acid in 50 cc. of sulfuric acid (1 : 1) and dilute to a liter. Determine the strength of this stock solution by precipitation of 100 cc. with ammonia. Calculate the dilution required to yield a standard solution containing 0.0002 gram of titanium per cc. Remove the requisite quantity of the stock solution and dilute according to the calculation. Finally check the strength of the standard solution by precipitation of 100 cc. with ammonia.

TITANIUM IN IRON AND STEEL

When titanium exists in iron or steel above 0.02 per cent it may be readily determined in less than 1/2 hour by the color method to be described. When present in smaller amount it may be determined with great precision by the writer's more refined color method requiring an ether separation of iron.

PROCEDURE FOR TITANIUM ABOVE 0.02 PER CENT

Put two grams each of the titanium steel and a non-titanium steel into 300 cc. Erlenmeyer flasks. Pour into each flask 80 cc. of sulfuric acid (1 : 3) and heat on a hot plate to complete solution. To each add 4 cc. of nitric acid (sp. gr. 1.2) and continue boiling until the solutions are free of fumes; cool. Transfer the solution of non-titanium steel to a comparing tube, using as little wash water as possible. Pour the test sample into the companion tube and dilute to the same volume as the other. Now observe if the two solutions have colors of the same character and depth, as they should. If the test sample be cast iron, filter the solution into the tube, preferably using a small wad of absorbent cotton because of gelatinous silica. Match the color with that of the non-titanium steel solution. Owing to the fact that cast iron contains a much larger percentage of metaloids than steel, it is usually found that the volume of the iron solution is a trifle less than that of the non-titanium steel when the colors match. In this case discard sufficient of the non-titanium steel solution to make the volumes equal.

Having obtained solutions showing the same color in equal volumes, introduce into each 2 cc. of 3 per cent hydrogen peroxide. Mix, and observe closely if the test solution shows any deepening of color. If titanium be present in as small an amount as 0.02 per cent, this deepening will be in evidence. It may even be detected with 0.01 per cent present, but in that case it is better to rely on the more refined method to be described.

Titanium if shown to be present in notable quantity is determined by adding from a burette a sufficient

amount of standard titanium solution to the solution of non-titanium steel to imitate the color of the test solution. If but two or three cc. are required, the amount used may be accepted as representing the amount in the test solution without further concern. But if more is required, the equality of volume of the two solutions, so vital to accurate results, must be restored before final comparison. When colors match at equal volumes, the amount of standard titanium solution used indicates the amount of titanium in the test sample.

When the material analyzed is *cast iron*,¹ the insoluble residue retains a small amount of titanium. For ordinary technical purposes this may be neglected. But if an accurate determination is desired, burn the insoluble in a platinum crucible, volatilize silica with hydrofluoric acid and 8 drops sulfuric acid (1 : 1), fuse residue with 1 gram sodium carbonate, dissolve out in dilute sulfuric acid and add to the main solution.

PROCEDURE FOR TITANIUM BELOW 0.02 PER CENT

The fact that titanium does not alloy readily with iron often results in the production of a material in which titanium, though employed in the process of manufacture, exists in minute quantity. This circumstance led the writer to cast about for some better means of determining these small amounts than has heretofore been available. The method below requires about an hour and a quarter, but is very useful when a report more satisfactory than the conventional "trace" is desired.

Weigh 2 grams of a non-titanium steel and the same quantity of the test sample. Place in dishes, add 50 cc. strong hydrochloric acid and heat to complete solution. Add to each 4 cc. nitric acid (sp. gr. 1.2) to oxidize iron. Evaporate each solution to about 10 cc., pour into separatory funnels, and wash the dishes with hydrochloric acid (2 parts strong acid, 1 part water). The total solution in the funnels should be in each case about 25 cc. Add cautiously to each, 50 cc. ether (free of alcohol), shake under a hydrant, and allow the two solutions to separate. Draw off the lower solutions into 400 cc. beakers, making the separation with care so that not more than a drop of the ethereal solution passes into the beaker in either case. It is essential to conduct these ether separations with the twofold purpose of having the minimum amount of iron in the acid solutions and of having the iron content of the acid solutions nearly equal.

Dilute each solution with 225 cc. hot water, add ammonia in slight excess, and boil. Allow the precipitates to settle and filter through 11 cm. filter papers. Wash thoroughly with hot water to remove chlorides.

Open the two filter papers into dishes, tearing off that portion of the filter paper which holds no precipitate. Pour over each 10 cc. of sulfuric acid (1 : 3). Rock the dishes until the precipitate has all dissolved. Filter each into 30 cc. comparison tubes, using small funnels and .7 cm. filter papers. This filtration may be dispensed with, but it is best to re-

move paper fiber. Wash the dishes and pass the washings through the filters. The total solution and washings in each instance should be equal in volume, between 15 and 18 cc.

The solutions now have a light maroon color, depending on the amount of iron present. Into each tube introduce 3 cc. 3 per cent hydrogen peroxide and mix. The maroon color is discharged, leaving the solution practically colorless in the case of the non-titanium steel. But if the test solution contains the most minute quantity of titanium, its presence is revealed by a residual lemon-yellow color. Even though the amount present is so extremely small that the usual manner of comparison leaves the operator uncertain of its presence, a glance through the solution from the top, holding the tube about $\frac{1}{2}$ inch above a white surface, instantly dispels all doubt. If there is as little as 0.001 per cent titanium present, the contrast between the pale green of the non-titanium solution and the yellowish tinge of the test clearly indicates that fact.

By adding the standard titanium solution to the solution of non-titanium steel the percentage of titanium is readily determined.

If the sample is *cast iron*, dissolve it in hydrochloric acid, filter and burn the residue in a platinum crucible. Volatilize silica with hydrofluoric acid and a few drops sulfuric acid, fuse residue with 1 gram sodium carbonate, dissolve out in hydrochloric acid, add to the main solution, and proceed with the ether separation. The insoluble residue can not be neglected when material is being examined for small amounts of titanium.

LIMA LOCOMOTIVE CORPORATION
LIMA, OHIO

VANADIUM IN STEEL BY THE HYDROGEN PEROXIDE COLOR METHOD

By C. R. McCABE

Received March 6, 1913

In 1911, the writer published the details of his original colorimetric method for vanadium in iron and steel¹—a method carefully devised to meet the difficulties occasioned by presence of titanium or molybdenum. Since these conditions are rarely encountered, a more direct and expeditious plan has been substituted for general use. It requires only twenty minutes when chromium is absent, and about double that time when it is present. Results are entirely satisfactory, as many experiments have shown.

The known rules governing all color methods are of unusual importance in the colorimetric vanadium determination. The large sample necessary renders the iron color deep enough to influence the vanadium color very materially. The determination is further limited by the sensitive character of the vanadium color with hydrogen peroxide, it being affected by the acidity of the solution. With the strength of acids commonly used in analytical work, the acidity may be satisfactorily controlled by means of the ordinary measuring apparatus. An excess of hydrogen peroxide partially bleaches the color after having pro-

¹ Cast iron samples should be passed through a 60-mesh sieve.

¹ Chem. Eng., 13, 243.

duced it. Also it is only when vanadium is in the quinivalent state that hydrogen peroxide imparts to its solution an immediate lasting color.

It is impossible to employ standard steels for the colorimetric vanadium determination with satisfactory results. For this reason the writer has devised a plan which consists in treating a non-vanadium steel precisely like the test, then imitating the color of the test by addition of a standard vanadium solution to the solution of non-vanadium steel, final comparison being made at equal volumes.

STANDARD VANADIUM SOLUTION

The vanadium pentoxide employed in making up the standard vanadium solution may be prepared in the laboratory, though it can now be obtained in the market.

Select a good grade of vanadate of iron containing about 60 per cent V_2O_5 , 38 per cent Fe_2O_3 , and 2 per cent SiO_2 ; put 5 grams of it into a beaker, add 100 cc. strong hydrochloric acid, and heat until dissolved. Add 20 cc. water and 1 cc. hydrofluoric acid. Filter from the slight insoluble residue, using a large filter paper and ribbed funnel. Pour into a separatory funnel, add 50 cc. ether, and shake under a hydrant. Allow the two layers to separate completely. Draw off the acid solution into a beaker, and discard the ethereal solution. Continue the extraction until the solution is free of iron as shown by the potassium sulfocyanide and ether test. Dilute to 400 cc., filter into an 800 cc. beaker and pass air through to remove the ether. Boil on a hot plate and add about 10 grams of potassium chlorate to oxidize the vanadium reduced by the hydrochloric acid. Then add in small quantities sufficient potassium carbonate to neutralize the greater part of the acid. When the proper degree of acidity is reached, a heavy precipitate of hydrated vanadic acid is thrown down. Filter through an 11 cm. filter paper, wash with hot water, and apply suction. Remove the cake, place on a watch glass and dry at $100^\circ C$. Several hours may be necessary to affect complete dehydration. Pulverize the vanadium pentoxide and preserve in a vial.

Place about 0.2 gram of the vanadium pentoxide in a small beaker. Add 30 cc. nitric acid (sp. gr. 1.2) and warm until dissolved. Dilute so that 1 cc. contains 0.0002 gram vanadium, or an amount corresponding to a 0.01 per cent when a two-gram sample is taken for analysis.

VANADIUM IN THE ABSENCE OF CHROMIUM

Place 2 grams of the vanadium steel and the same quantity of a non-vanadium steel in 300 cc. Erlenmeyer flasks. Add exactly 40 cc. nitric acid (sp. gr. 1.2) to each and heat until the steel is dissolved. To each add about 0.1 gram potassium permanganate and digest for two minutes. Then add dilute ammonium bisulfite in sufficient quantity to clarify the solution, and continue heating until SO_2 is all expelled: by this operation carbon is oxidized.

Cool the solutions in running water and transfer to comparing tubes. Bring to equal volumes if they are not already so, and mix. Observe the colors,

which should be of the same character and depth.

Into each tube introduce exactly 1 cc. 3 per cent hydrogen peroxide. Mix the test solution, and observe the vanadium color to gain an approximate idea of the vanadium content of the test.

To the solution of non-vanadium steel add, from a burette, as much of the standard vanadium solution as it is thought may be safely used without passing the amount existing in the test solution. To the test solution add an equal amount of water. Mix the solutions and compare colors. If the test solution appears darker, as will be the case if the proper precaution has been observed, add a further quantity of standard vanadium solution to the non-vanadium steel solution. Add an equal quantity of water to the test solution to maintain the equality of volume. Mix, and again compare. Continue in this manner until the colors match at equal volumes. The amount of standard vanadium solution used indicates the result. Thus, if 20.5 cc. standard vanadium solution are used, the result is 0.205 per cent vanadium.

VANADIUM IN THE PRESENCE OF CHROMIUM

When a vanadium steel contains chromium its color must be compensated to secure a satisfactory comparison. The uncertain color of chromium salts, which varies with the acidity of the solution and other causes not readily determined, renders worthless some apparently simple methods of compensation. The only plan which proved satisfactory, after many experiments, is as follows:

Weigh 2 grams of the chrome-vanadium steel and an equal amount of a plain steel, placing in 400 cc. beakers. Weigh with great care an amount of potassium bichromate corresponding to the chromium content of the test steel and place it in the beaker containing the plain steel. To each add 80 cc. sulfuric acid (1 : 3), and heat.

When nearly in solution, add to each 25 cc. of strong nitric acid and heat for ten minutes. Vanadium is not completely oxidized by a small amount of nitric acid such as would oxidize the iron.

Cool the two solutions in running water, introduce into comparing tubes, and bring to equal volumes. Mix, and observe the colors. Owing to possible error in the chromium determination it is doubly important to know that the solutions show colors of the same character and depth at equal volumes before proceeding with the analysis.

The determination is now finished as when chromium is absent.

For vanadium steels as they commonly occur, this method as described is entirely satisfactory. But when the determination is embarrassed by presence of titanium or molybdenum, or when the equally troublesome case of a steel containing a small amount of vanadium with much chromium presents itself, the more elaborate method mentioned in the first section of this paper may be employed. That method, though it requires more time, has been found to be thoroughly reliable under adverse conditions.

THE DETERMINATION OF ZINC IN TREATED TIES

By FRANCIS C. PRARY AND M. GORDON MARTIN

Received June 16, 1913

It was recently stated in THIS JOURNAL that over nine million ties were treated with zinc chloride in 1911. The railroads are said to be having excellent results with these in practice, and are buying large quantities of them, mostly on a specification of one-half pound of zinc chloride per cubic foot, which means about 0.5 per cent of metallic zinc.

The determination of this small amount of zinc in such material necessitates the use of a rather large sample and the complete destruction of the organic matter. The method commonly used is said to have originated in the laboratories of the Union Pacific Ry., and consists in charring the sample by heating with a small amount of concentrated sulfuric acid, and then adding nitric acid, a few drops at a time, continuing the heating until all organic matter is destroyed and nitrous fumes driven off. The solution is then diluted, iron removed, the zinc precipitated as sulfide and determined in the usual manner as oxide.

This method is said to give satisfactory results with ties except those of oak. Red oak ties in particular are impossible to analyze by this method, for the treatment with acids, no matter how prolonged, will not destroy all the organic matter, but leaves the solution dark colored, and the precipitation of the zinc is so incomplete that less than half of that present is found. In some determinations which we made by this method on the red oak shavings used in the work herein described, we found that the zinc sulfide was precipitated in such a finely divided form that it was not retained by two thicknesses of C. S. & S. white band No. 589 paper, one thickness of which will retain barium sulfate completely.

This difficulty was brought to our attention by Mr. H. M. Newton, of the Kettle River Co., to whom we are indebted for the details of the method of analysis given above and the method of Mr. Stenger, described later. We are also indebted to him and to the Kettle River Co. for furnishing us half of an untreated red oak tie and another half-tie which had been treated "to refusal" with a 4 per cent solution of zinc chloride. The standard method of sampling such material is by boring with a fine one-inch bit, at a point two feet from the end of the tie. To obtain a large quantity of material of about the fineness of such a sample, we sawed the half-tie in two, and reduced half of one of these pieces to shavings by means of a shaper in the university shop. Similar shavings were taken from the untreated half-tie for use with known amounts of zinc.

It is a well-known fact that oxalic acid is made by heating wood shavings or sawdust with caustic alkali, and that care must be taken in the process not to allow the temperature to reach too high a point, or the reaction will be too violent and the acid will be destroyed. It was believed that it would be possible to completely destroy the organic matter in red oak shavings in this way, and it was found that such destruction was both easy and rapid if the process was

properly conducted and a little potassium nitrate added toward the last. The fusion can not be made satisfactorily in an iron dish, as some ferrocyanide is usually formed from the iron of the dish during the fusion, and so much iron goes into solution that its separation becomes tedious. By using a nickel dish, very little of the metal is dissolved, and that can be easily and quickly removed.

The process which has given us the best results is as follows: Two grams of the dried shavings are weighed into a 200-300 cc. nickel dish, moistened with a little water, and heated gently to insure thorough saturation with the water. Two sticks (about 30 grams) of pure potassium hydroxide are now added, and the mixture heated cautiously until the hydroxide is melted. The mass must now be stirred thoroughly with a pure nickel wire, and the heat increased so that it boils vigorously. As the water is boiled off, the fusion becomes almost a salmon-pink (with red oak) and lumps of a gummy substance appear on the surface. As the boiling is continued, these masses disappear, seeming to dissolve, and the color changes to a yellowish brown. The fusion now begins to foam a good deal, and must be continually stirred. When spurts of inflammable gases appear, and the mass is rather viscous, the addition of the nitrate is begun. A piece of potassium nitrate the size of a grain of wheat is added, and the heating and stirring continued about a minute, repeating the addition, heating and stirring as often as may be necessary. The fusion becomes more fluid and lighter in color as the nitrate is added. Usually about half a gram of nitrate will be required.

When all organic matter is oxidized, the fusion becomes perfectly transparent, colorless, and quiet; the dish is then inclined so as to wash down the sides with the fused mass and get any material that might be lodged there and escape oxidation. After cooling, the mass is dissolved in water, 15 to 20 cc. of bromine water added, and the whole boiled about a minute. The nickelic oxide thus precipitated is filtered off on a Gooch crucible, and the filtrate and washings transferred to a 750 cc. casserole and made barely acid with concentrated hydrochloric acid. Sodium sulfite is added, a little at a time, until the first violent effervescence ceases, and then enough hydrochloric acid added to make the amount of free concentrated acid from 2 to 6 per cent of the final volume. Dilute to about 400 cc., heat to boiling, and titrate with potassium ferrocyanide, using a saturated solution of uranium nitrate on a spot plate as an indicator. The conditions for the titration are the same as for any such determination of zinc; the necessary blank must be determined and subtracted from the burette reading.

For use with a sample of the size mentioned, we prefer a solution of about 5 grams potassium ferrocyanide per liter, which is equivalent to about 1 mg. of zinc per cc. The blank with such a solution was found to be about 4 cc., the end point being very satisfactory.

Enough sulfite must be used to reduce all oxidizing compounds present, to prevent them from decom-

posing the ferrocyanide, and care should be taken to keep the volume of the solution and its acidity about as above stated. With practice the fusion can be made in about ten minutes and the whole determination in half an hour. We prefer to standardize our solutions with zinc oxide, made by evaporating a little of a solution of C. P. zinc sulfate in a weighed platinum dish, blasting a few minutes to remove all sulfur compounds, cooling and weighing. The same volume should be used in the standardization as in the regular determination, and about 10 grams of ammonium chloride or 40 grams of potassium chloride added to make the conditions the same, for it is well known that variations in the conditions change the value of the ferrocyanide solution.

Using this method, on the dried shavings from the treated tie, we obtained the following results in eight consecutive determinations: 0.881, 0.901, 0.891, 0.905, 0.896, 0.886, 0.901, 0.891 per cent metallic zinc. Using the untreated shavings, and adding to each determination a solution containing 0.0255 gram of zinc as chloride, the following amounts of zinc were found: 0.0253, 0.0251, 0.0250, 0.0252, 0.0253 gram. There is apparently a slight loss of zinc, probably due to spattering during fusion, being only about 0.02 per cent by weight of the original sample of shavings.

It is not essential to the success of this method that the zinc be determined by titration; after removing the nickel and the bromine it may, of course, be determined by any other method if desired.

So far as we were able to determine at the time this work was taken up, the only other satisfactory method for this determination was an electrolytic one devised by Mr. L. A. Stenger, of the Twin City Rapid Transit Co., of this city, and used in their laboratory. Mr. Stenger describes his method as follows:

"Five to 10 grams of borings or sawdust are taken, about 150 cc. pure water added, then 6 to 8 grams of sodium hydroxide. The mixture is heated nearly to boiling for a few minutes, then electrolyzed with a rotating platinum anode and silver-plated copper cathode for about forty minutes. The cathode area is about 250 sq. cm., and a current of about 5 amperes at six volts is employed. A tall 400 cc. beaker is used to allow some space for frothing, which can be prevented by addition of ether if desired. The cathode with the zinc deposit is removed quickly, washed with hot water and alcohol and dried. After weighing, it is replaced in the solution and the electrolysis continued for five to ten minutes. If little or no increase in weight is found, deposition is considered complete."

Mr. Stenger very kindly determined zinc in a sample of our dried shavings by the above method, and found 0.88 per cent, which is in good agreement with our results. He also tried our method as above outlined on the same sample, and on tamarack and red oak ties, one of which had been treated with both creosote and zinc chloride, and states that the method worked very well.

While we were working on this method, it was found in the laboratory of the Kettle River Co. that complete

oxidation of the wood could be obtained, even with red oak, by using potassium chlorate with the nitric and sulfuric acids in the ordinary method. Mr. Newton very kindly had their laboratory make two determinations on our sample by this method, the results being obtained 0.91 and 0.92 per cent zinc. It is evident that the agreement is as close as could be expected.

We believe that this method of fusion with alkali is adapted for the determination of minute amounts of metals in the presence of large amounts of organic matter of any sort, and have tried it on the determination of tin in canned goods, with success. A larger sample can, of course, be used if a larger nickel dish is at hand.

UNIVERSITY OF MINNESOTA
MINNEAPOLIS

HICKORY NUTS AND HICKORY NUT OIL

By GEORGE O. PETERSON AND E. H. S. BAILEY

Received June 26, 1913

Since the hickory nut crop of the United States is a large one, although no accurate statistics exist in regard to it, it has seemed to us worth while to make a preliminary study of the properties of the oil. The genus *carya* of the walnut or *juglandaceae* family comprises eight species, only two of which, the *carya ovata* or shellbark hickory and the *carya amara* or swamp hickory are here considered. The shellbark nuts are of such commercial value that their oil could hardly be extracted with profit if intended for ordinary table use. The swamp hickory nuts and those called "pig nuts" are abundant and at present not utilized, except as food for hogs and squirrels.

Work on the composition of nuts has been carried on especially in the Iowa,¹ California² and Maine³ Agricultural Experiment Stations, and from two of these the analyses of hickory nuts (presumably *C. ovata*) are presented for comparison with our own analysis.

TABLE I—CHEMICAL COMPOSITION OF HICKORY NUTS

	Iowa Sta.		P. and B.
	Maine Sta.	meats	meats
Refuse.....	62.2(a)	68.0	62.8
Edible portion.....	37.8	30.0	37.2
Water.....	1.4	3.97	3.45
Protein.....	5.8	20.5	13.2
Fat.....	25.5	64.6	70.2
Carbohydrates.....	4.3
Ash.....	0.8	2.2	1.73
Fuel value per pound in calories.....	1265	3226 (calc.)	3310 (calc.)
Crude fiber.....	..	2.3	2.0
N-free extract.....	..	6.40	9.42

(a) Per cents in this column refer to whole nuts.

The methods of analysis used were in general those of the "Official and Provisional Methods of Analysis," *Bull.* 107, Bur. of Chem., U. S. Dept. of Agr., with such modifications as seemed expedient. All desiccations were carried out in air instead of hydrogen.

HICKORY NUT OIL

In extracting the oil from the meats it was decided to use the pressure method rather than the extraction

¹ "The Chemical Composition of Nuts Used as Food," *Proc. Ia. Acad. Sci.*, 10, 108-11.

² "Nuts and Their Use as Food," *Farmers' Bull.* No. 332.

³ *Maine Agr. Expt. Sta.*, 1899, 87.

method, as the former is the commercial method, and the only one used for extracting edible oils. For extracting the oil a cylindrical press was constructed by using an iron cylinder with an inside diameter of $3\frac{1}{4}$ inches and a height of 7 inches into which was fitted a close-fitting piston. The cylinder was set on an iron plate perforated with several $\frac{1}{8}$ inch holes, and holes were drilled in the cylinder near the lower end to facilitate the running out of the oil. When hydraulic pressure was applied to the piston the oil exuded from the holes and collected in a metal pan in which the press had been placed. A pressure of 150 to 300 atmospheres was applied to the piston. A second pressure was applied to the material after breaking up the press cake and heating the press and the press cake to 50–60° C. The following table shows the yield of oil from the various samples, the total per cent of oil present, and the actual per cent of oil extracted:

TABLE II

Kind of sample	Yield in per cent	Total per cent of oil present	Per cent of oil present extracted
<i>C. Ovata</i> —Whole, cracked, cold-pressed.....	15.8	26.5	59.5
Hot-pressed.....	2.0	..	7.5
<i>C. Ovata</i> —Meats alone cold-pressed.....	30.6(a)	70.2	42.7
Hot-pressed.....	17.5	..	23.2
<i>C. Amara</i> —Whole, cracked, cold-pressed.....	22.1
Hot-pressed.....	3.8

(a) Only 100 atmospheres pressure.

The oils, as at first obtained, were cloudy, and the hot-pressed were darker than the cold-pressed. After filtration through filter paper the oils became bright and clear, and were of the appearance and consistency of Italian olive oil. They possessed an agreeable hickory nut odor and flavor.

The following table gives the constants as obtained from both these oils and for comparison those obtained at the Maine Experiment Station.¹

TABLE III—CONSTANTS OF HICKORY NUT OILS

	<i>C. amara</i>	<i>C. ovata</i>	Maine Expt. Sta.
Specific gravity at 24° C.....	0.9119	0.9119	0.9164
Refractive index at 20° C.....	1.4699	1.4699	1.4696
Hehner number.....	95.6	95.7	..
Reichert-Meißl number.....	0.48	0.47	..
Iodine value.....	105.2	106.8	102.8
Saponification value.....	190.0	189.6	..

The similarity of the two oils is very evident. Perhaps the most important factor for comparison of the different classes of oils is the iodine value, for this is a measure of the unsaturated glycerides present, and thus determines whether the oil is drying, semi-drying or non-drying. The iodine value here obtained for hickory nut oil seems to classify it with the semi-drying oils. Here belong cottonseed oil, corn oil, rape seed oil, Brazil nut oil, and beech nut oil. In the following table is shown a comparison of constants of hickory nut oil with those of cottonseed oil and those of the non-drying oil, *viz.*, olive oil.

These figures show that hickory nut oil resembles very closely cottonseed oil, and would be difficult to distinguish from it.

The hickory nut oil is very agreeable as a salad oil,

¹ *Loc. cit.*

TABLE IV

	Hickory nut oil	Cottonseed oil	Olive oil
Specific gravity.....	0.9119 at 24° C.	0.9203 at 19° C.	0.9100 at 24° C.
Refractive index.....	1.4699 at 20° C.	1.4748 at 15° C.	1.4670 at 20° C.
Iodine value.....	106.0	106.0	82.0
Saponification value.....	190.0	192.0	190.0
Reichert-Meißl number.....	0.48	..	0.6
Hehner number.....	95.7	95.6	95.4

so that if it can be obtained at a sufficiently low cost, it can be used for this purpose. The *C. amara* or the *C. porcine* (pig nut), which are now considered as absolutely of no value, would yield at least a gallon and a half of oil per bushel and the nuts need only be crushed before they are pressed.

SUMMARY

- I. The food value of hickory nuts is high.
- II. The oils from the two species of hickory nuts, *C. ovata* and *C. amara*, are practically identical and are similar to cottonseed oil.
- III. The oil retains the flavor of the hickory nut, and is practically equal to olive oil.
- IV. The possibility of extracting the oil on a commercial basis should be further investigated.

CHEMICAL LABORATORIES
UNIVERSITY OF KANSAS
LAWRENCE

THE ANALYSIS OF MAPLE PRODUCTS I

AN ELECTRICAL CONDUCTIVITY TEST FOR PURITY OF MAPLE SYRUP¹

By J. F. SNELL

The most commonly used adulterant of maple sugar is granulated sugar, which is, of course, chemically identical with the predominating constituent of the pure material. For the detection of such adulteration we are dependent upon measurements of the small quantities of the non-sugar constituents, the percentages of which in the syrup are necessarily decreased by the addition of the practically pure sucrose, together with the proportional quantity of water necessary to convert it into a syrup. The ash, the soluble and insoluble ash, the alkalinities of these, the malic acid value, and the amounts of precipitate produced by lead subacetate and by normal lead acetate are alike lowered by such adulteration, though not necessarily in proportion to the amount of adulteration.²

Sucrose being a non-conductor of electricity, and the salt constituents conductors, it is reasonable to

¹ This test was described at the Washington meeting of the American Chemical Society in December, 1911, but publication was deferred until further experiments could be made, particularly (1) upon the effect of adulteration on the conductivity value and (2) upon the relation between the conductivity of the syrup and that of its ash solution. This later experimental work has been carried out under my direction by Mr. J. M. Scott, to whom my thanks are due for very competent assistance. This assistance was rendered possible by the Dominion Government Grant for the Advancement of Agriculture. Through the courtesy of Prof. Frank T. Shutt, M.A., F.R.S.C., the present paper was read before the Royal Society of Canada at Ottawa, May 28, 1913.

² The effect of such adulteration upon the various analytical values will be discussed in a later paper.

anticipate that maple syrups adulterated with granulated sugar in more than very small quantities will show materially lower conductivities than pure maple syrups. Since with suitable apparatus a measurement of electrical conductivity can be made in a few seconds, a method based upon such a measurement would have a decided advantage in point of rapidity over any of the methods now in vogue.¹

The most rapid methods hitherto proposed have depended upon precipitation with lead subacetate and measurement of the volume of the centrifugally-settled precipitate.² No great delicacy has been claimed for these methods, and even they require more time than a conductivity measurement.

THE CONDUCTIVITIES OF UNDILUTED PURE SYRUP

Measurements of the conductivities of the undiluted syrup have been made upon 43 samples, all of Canadian origin. Eleven pairs of early and late products from the same or adjoining woods were sent me by the makers from various parts of the Province of Quebec in the season of 1911. Thirteen samples from Ontario and six from Quebec, all of the season of 1911, were kindly forwarded by Dr. Anthony McGill, Chief Analyst of the Inland Revenue Department, Ottawa, as fairly representative of the 450 odd samples collected by the Department for the purpose of establishing a standard of purity for maple syrup. Each of these was accompanied by a declaration of genuineness signed by the maker.³

The remaining two samples of the 43 were made from identical sap, one by rapid boiling in a modern evaporator having a corrugated pan, the other in an iron kettle, not entirely free from rust, with very slow boiling.

TABLE I—SUMMARY OF DENSITIES AND CONDUCTIVITIES OF 42 GENUINE CANADIAN MAPLE SYRUPS

	Conductivity	
	Sp. gr. 15° C	$\kappa \times 10^5$ 25° C.
Mean.....	1.333	18.7
Minimum.....	1.305	9.6
Maximum.....	1.355	33.6
Percentage deviation of minimum from mean.....	2.1	49
Percentage deviation of maximum from mean.....	+1.6	+80

A summary of the variations of the specific gravity and of the electrical conductivity of 42 of these 43 syrups is given in Table I. The syrup omitted from this summary is one of the Inland Revenue Department samples, which was of extremely low density. Its specific gravity was 1.279, its moisture content (according to the analysis made in the Inland Revenue

¹ As long ago as 1889, E. Reichert, *Zeit. anal. Chem.*, **28**, 14 (1899), and more recently, Hugh Main, *International Sugar Journal*, **11**, 334 (1909), *Zeit. Ver. Zuckerind.*, **59**, 783 (1909); *Chem. Abstr.*, **3**, 2249 (1909) and A. E. Lange, *Z. Ver. Zuckerind.*, **60**, 359; *Chem. Abstr.*, **4**, 1554 (1910) have proposed methods of estimating the ash of sugars and syrups from their electrical conductivities. These methods appear to have given good results in the hands of their authors but have been adversely criticized by others. Reichert's, by Fock and Plath, *Zeit. Ver. Zuckerind.*, **39**, 710 (1889); Main's and Lange's, by A. Trenkler, *Oesterr.-und Zeit. Zuckerind.*, **39**, 437; *Chem. Abstr.*, **4**, 308 (1910).

² Hortvet, *J. Am. Chem. Soc.*, **26**, 1543 (1904); Bureau of Chem., U. S. Dept. Agr., *Bulletin* **107**, 72; Jones, Vermont Agr. Expt. Sta., *18th Annual Report*, 1906, 322.

³ See *Bulletin* **228** of the Laboratory of the Inland Revenue Department (1911). The syrups examined were Nos. 184-191, 193-195, 211-214, 263, 278, 281 and 284 of this bulletin.

Laboratory) 38.59 per cent, and its conductivity ($\kappa \times 10^5$) 45.0.

As a general rule, the syrups of high density showed low conductivities and those of low density showed high conductivities. This indicates that in undiluted syrups the concentration of the sugar has more influence upon the conductivity than has the concentration of the electrolyte components.

The syrup made in the iron kettle had a specific gravity of 1.326, and a conductivity of 25.9, while that made from the same sap by rapid, shallow boiling in an evaporator showed a specific gravity of 1.334, and a conductivity of 22.4. This is in harmony with the general rule of lower conductivity accompanying greater density. The minimum conductivity (9.6) was shown by the syrup of maximum density (1.355), while the maximum conductivity (33.6) was found in a syrup of density 1.311.

THE EFFECT OF DILUTION

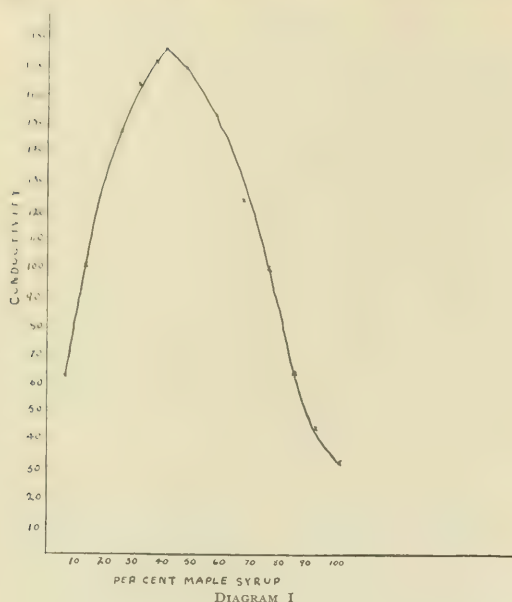
The results of the above measurements indicate that as the water-content of maple syrup increases, the conductivity increases. In other words, the more dilute the solution the greater the conductivity. This is not in line with the usual behavior of aqueous solutions of electrolytes. In general, the specific conductivity of such solutions decreases with dilution. The thought, therefore, suggested itself that if one continued to dilute maple syrup with water, a point of dilution must eventually be reached at which the conductivity would cease to increase and begin to decrease—a point of maximum conductivity. This proved to be the case, the maximum occurring at a dilution of one volume of syrup to two of water, *i. e.*, in a mixture containing $33\frac{1}{3}$ per cent of syrup by volume, or 39.6 per cent of syrup of normal density (1.320) by weight.

TABLE II—EFFECT OF DILUTION UPON CONDUCTIVITY OF SYRUP

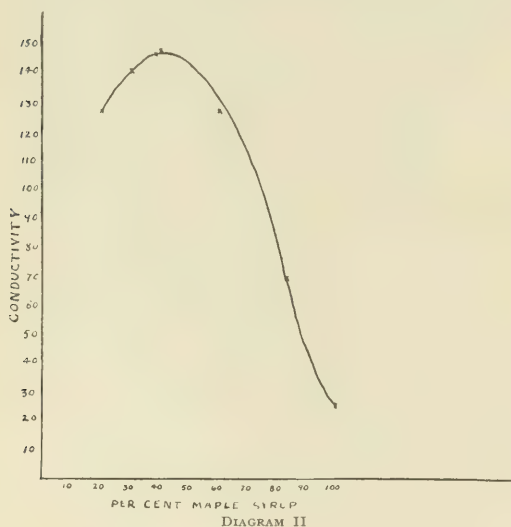
Syrup I		
Per cent maple syrup by volume	Per cent maple syrup by weight	Conductivity value
5	6.6	62
10	13.0	100
20	25.1	147
25	30.9	163
30	36.5	171
33 ¹ ₃	40.1	175
40	47.2	169
50	57.3	153
60	66.8	123
70	75.8	99
80	84.3	63
90	92.3	44
100	100.0	32

Syrup II	
Per cent maple syrup by weight	Conductivity value
20	127
30	141
39. ⁹	148
40	147
60	127
83 ¹ ₃	69
100	26

Table II and Diagrams I and II give results typical of the effect of dilution upon the specific conductivities of maple syrups.



On each side of the point of maximum conductivity there is a considerable range of concentrations, within which the conductivity differs very little from the maximum. This renders it possible to measure the maximum conductivity of diluted maple syrup without observing much precision in making up the mixture of maple syrup and water. This is a point of great practical advantage in relation to the rapidity of the method described below. It is not necessary to weigh the syrup nor to reduce it to a definite density.



An ordinary 25 cc. graduate can be used to measure the syrup, the two portions of water subsequently measured from the same graduate serving to rinse out the syrup which adheres to the sides.

The range of variation of the conductivity of pure maple syrups thus diluted with two volumes of water is much narrower than that of the conductivity of the undiluted syrups. The mean conductivity at 25° C. ($K \times 10^5$) of the diluted solutions of the 42 syrups of Table I was 153, or over 8 times the mean conductivity of the same syrups in the undiluted state. The minimum was 120, the maximum 203, the latter being the conductivity value of the syrup made in the iron kettle. The minimum deviates from the mean by 21 per cent, as against 49 per cent in the undiluted syrup; the maximum by 33 per cent, as against 80 per cent for the undiluted syrup. We have thus a total range of 54 per cent for the diluted as against 129 per cent for the undiluted syrup. The forty-third syrup, omitted from the summary in Table I, on account of its extremely low density and high conductivity, gave a perfectly normal conductivity value (167) when diluted with two volumes of water.

The maximum conductivity, or more strictly speaking, the conductivity of the mixture of one volume of syrup with two volumes of water is, accordingly, made the basis of the method here proposed.

METHOD

Measure out into a small beaker (or directly into the conductivity cell) a suitable quantity (15 cc.) of the syrup, allowing thorough draining. Using the same graduate, add two successive portions of water, each equal in volume to the syrup taken. Mix thoroughly, pour into conductivity cell, bring to 25° C., and make the measurement. Divide the constant of the cell by the observed number of ohms and multiply the result by 100,000.

Genuine syrups have given values of 110 to 200, but further experience may extend these limits a little.¹

Syrups giving conductivity values distinctly outside these limits may be condemned. Those giving normal values are not necessarily pure and should be further examined by well-established tests.

APPARATUS

The essential features of the apparatus are:

1. A low voltage electrical current operating an induction coil.
2. A conductivity cell of a form suitable for liquids of low conductivity, and with electrodes not easily displaced.
3. A Wheatstone bridge with telephone.
4. A device for exact regulation of temperature.

In the present work a Kohrausch Universal Bridge bearing the name plate of Messrs. Philip Harris & Co., Birmingham, England,² has been used. The induction coil with which this bridge is fitted was operated by two lead accumulators connected in series. A small Deveau telephone was found to give better results than a Bell. With this very convenient bridge and telephone there was no difficulty in obtaining a sharp minimum of sound. The conductivity cell used at first was of the form represented in Fig. 295 (p. 402)

¹ I have collected nearly 130 syrups of the season of 1913, direct from the sugar bushes of Ontario and Quebec and intend determining the limits of conductivity value in these both at 25° and at 20° C.

² No. 7072 in this firm's Physics catalogue, Vol. 1.

of Ostwald and Luther's "Physiko-chemiker Messungen," 2nd edition (1902). Its capacity was about 50 cc. It had electrodes of 2.5 cm. diameter set 1 cm. apart, which maintained their position satisfactorily,

Eimer & Amend, of New York. The platinum electrodes of this special cell are of B. & S. gauge No. 27, and are 3.2 cm. in diameter. They are adjustable as to distance, but are firmly held in position by set-

TABLE III—SYRUPS MADE IN LABORATORY SEASON OF 1912

No.	Date made	Saps	Density 15° C.	Dry matter from density	A Conductivity value	B Conductivity value, ash	C Total ash Dry basis	D Soluble ash Dry basis	E Insoluble ash Dry basis	F Alkalinity Total ash	G Alkalinity Soluble ash	H Alkalinity Insoluble ash
1	Apr. 6	Hard and soft	1.329	66.5	150		0.95	0.44	0.51	1.18	0.45	0.73
2	Apr. 7	Hard and soft	1.329	66.5	164	61	0.99	0.66	0.33	1.42	0.30	0.92
3	Apr. 10	Hard and soft	1.326	66.0	144	57	0.88	0.38	0.50	1.46	0.46	1.00
4	Apr. 11	Hard and soft	1.327	66.2	153	56	0.95	0.57	0.38	1.42	0.46	0.86
5	Apr. 12	Hard and soft, evaporated on steam bath	1.333	67.1	145	61	1.00	0.58	0.42	1.30	0.47	0.83
6	Apr. 12	Hard and soft, evaporated over flame	1.320	65.0	135	58	0.88	0.59	0.29	1.19	0.46	0.73
7	Apr. 13	Hard and soft	1.325	65.8	138	50	0.85	0.35	0.50	1.30	0.48	0.82
8	Apr. 15	Hard and soft	1.325	65.8	152	68	0.91	0.52	0.39	1.11	0.45	0.66
9	Apr. 18	Hard and soft	1.327	66.2	135	50	0.88			1.41	0.43	0.98
10	Apr. 23	Hard and soft	1.320	65.0	119	48	0.95	0.43	0.52	1.18	0.36	0.82
11	Apr. 25	Hard and soft	1.329	66.5	126	54	0.98	0.50	0.48	1.31	0.47	0.84
12	Apr. 29	Hard and soft	1.327	66.2	155	58	1.09	0.46	0.63	1.61	0.49	1.12
Average results for mixed saps.					143	56	0.94	0.50	0.45	1.32	0.46	0.86
Percentage deviation maximum from mean					14.7	21.4	15.9	32.0	40.0	10.6	8.7	30.2
Percentage deviation minimum from mean					16.8	14.3	6.4	30.0	35.6	15.9	21.7	23.3
13	Apr. 15	Hard	1.322	65.4	145	48	0.87	0.41	0.46	1.17	0.41	0.76
14	Apr. 16	Hard	1.327	66.2	152	57	1.00	0.49	0.51	1.29	0.46	0.83
15	Apr. 20	Hard, evaporated over flame	1.322	65.4	146	54	1.02	0.47	0.55	1.39	0.50	0.89
16	Apr. 20	Hard, caramelized in boiling	1.319	64.9	148	50	0.97	0.60	0.37	1.28	0.45	0.83
17	Apr. 22	Hard	1.330	66.6	148		1.05	0.48	0.57	1.55	0.52	1.03
18	Apr. 24	Hard	1.325	65.8	141	57	0.96	0.45	0.51	1.45	0.47	0.98
19	Apr. 24	Hard	1.325	65.8	137	52	0.94	0.38	0.56	1.23	0.42	0.81
Average results for hard sap syrups.					145	53	0.97	0.47	0.50	1.34	0.46	0.88
Percentage deviation maximum from mean.					4.8	7.0	8.2	27.7	14.0	15.7	13.0	17.0
Percentage deviation minimum from mean.					5.5	9.4	10.3	19.1	26.0	12.7	10.9	13.6
20	Apr. 16	Soft	1.321	65.2	134	54	0.90	0.47	0.43	1.18	0.40	0.78
21	Apr. 20	Soft	1.322	65.4	135	58	0.81	0.42	0.39	1.10	0.44	0.66
22	Apr. 22	Soft	1.330	66.6	148		0.92	0.54	0.38	1.27	0.55	0.72
Average results for soft sap syrups.					139	56	0.88	0.48	0.40	1.18	0.46	0.72
Percentage deviation maximum from mean.					6.5	3.6	4.4	12.5	7.5	7.5	19.6	8.3
Percentage deviation minimum from mean.					3.6	3.6	8.0	12.5	5.0	6.8	13.0	8.3
General average.					143	55	0.94	0.49	0.46	1.31	0.46	0.85
Maximum.					164	68	1.09	0.66	0.63	1.61	0.55	1.12
Minimum.					119	48	0.81	0.35	0.29	1.10	0.36	0.66
Percentage deviation maximum from mean.					14.6	23.6	16.0	30.6	37.0	22.9	19.6	31.8
Percentage deviation minimum from mean.					16.8	12.7	13.8	28.6	37.0	16.0	21.7	22.4

TABLE IV—FULL ANALYTICAL DATA FOR TWELVE SYRUPS OF TABLE I

Number	Run	A Conductivity value	C Total ash Dry basis	D Soluble ash Dry basis	E Insoluble ash Dry basis	F Alkalinity Total ash	G Alkalinity Soluble ash	H Alkalinity Insoluble ash	Canadian Lead No.	Modified Winton Lead No. (a)
1	Early	133	0.80	0.46	0.34	1.04	0.46	0.58	3.36	1.74
2	Early	149	0.82	0.59	0.23	1.01	0.58	0.43	3.10	2.11
3	Early	152	0.89	0.61	0.28	1.05	0.53	0.52	2.95	2.04
4	Early	139	0.86	0.61	0.25	0.93	0.48	0.45	2.82	1.85
5	Early	147	0.78	0.50	0.28	0.89	0.45	0.44	2.93	1.96
6	Early	145	0.89	0.58	0.31	1.08	0.56	0.52	3.30	2.18
7	Early	139	1.09	0.61	0.48	1.03	0.51	0.52	2.64	1.56
8	Early	162	1.14	0.79	0.35	1.20	0.64	0.56	3.39	2.33
9	Late	187	1.38	0.93	0.45	1.63	0.91	0.72	3.29	2.04
10	Late	149	0.86	0.57	0.29	1.12	0.56	0.56	3.44	2.40
11	Late	138	0.89	0.60	0.29	1.01	0.50	0.51	2.70	2.10
12	Late	158	1.14	0.62	0.52	1.14	0.54	0.60	3.62	1.88
Average.		150	0.96	0.62	0.34	1.10	0.56	0.53	3.13	2.02
Per cent deviation of maximum from mean		24.7	13.8	50.0	52.9	48.2	62.8	35.8	15.6	18.8
Per cent deviation of minimum from mean		11.3	18.8	28.8	32.4	19.1	17.9	18.9	15.6	22.8

(a) Determined upon 25 g. dry matter instead of upon 25 g. syrup. *Bull.* 228, Laboratory of the Canadian Inland Revenue Department

as was demonstrated by repeated determinations of the cell constant. Later, a special cell of the same type with extra heavy electrodes and with a thermometer set in the cover was made for me by Messrs.

screws. The thermometer range is 20° to 30°, graduated in tenths. This type of cell has proved perfectly satisfactory for the purpose.

In routine work it might be advisable to have a

considerable number of cells fitting the same pair of electrodes. These could be filled with the different samples and set in a thermostat to come to the required temperature, when measurements of all could be made in rapid succession. I have not used a thermostat in this work, but have regulated the temperature by placing the conductivity cell in a beaker of water of a suitable temperature, a fraction of a degree above or below that desired, and stirring the contents of the cell with the electrodes until the thermometer within the cell showed the correct reading.

The cell constant was determined by use of 0.1, 0.02 and 0.01 M potassium chloride solution, made up at 18° C. from the ignited C. P. salt, assuming for these¹ at 25° C. the conductivities 1289, 276.8 and 141.2×10^{-6} .

RANGE OF VARIATION OF THE CONDUCTIVITY VALUE IN GENUINE SYRUPS

In addition to the 43 syrups referred to above, the conductivity value has been determined on 22 syrups made in this laboratory in the season of 1912 (see Table III). These syrups were all made from the sap of ten trees in the woods of the Macdonald College farm—six hard and four soft maples. They represent the runs of different days from April 6th to April 29th; some were made from the sap of the soft maples alone, others from the hard maples only, though the majority represent the mixed sap of the ten trees. They were boiled down in basins on gas stoves with the exception of one (No. 5), which was evaporated on the steam bath. These 22 syrups show a range of 119 to 164, average 143. This is a total range of 31.4 per cent. This is about the same range of variation as is shown by the total ash, and a much lower range than those shown by the soluble ash, the insoluble ash and the alkalinities.

Table IV includes analytical data for twelve of the Quebec syrups included in the summary given in Table I. These were examined to determine whether this apparent advantage of the conductivity method held for syrups of various origin, as well as for those from a single bush. It will be seen that among these 12 syrups the range of the conductivity value is much narrower than that of the total ash and narrower also than that of any of the other data except the Canadian lead number.

If this narrowness of range shall be found to be characteristic of the conductivity values of pure maple syrups in general, it will be a point of advantage for this method.

I have also examined three syrups made at the Vermont Agricultural Experiment Station under the supervision of Prof. C. H. Jones, who advised me that they were prepared with great care, "every opportunity being given for the malate of lime to settle out." These syrups were exceptionally light in color. As received, they were of exceptionally high density, as indicated by Prof. Jones' refractometer readings, *viz.*, No. 1 at 24.75° C., 1.4632; No. 2 at 21.5° C., 1.4651; No. 3 at 24.75° C., 1.4623. For my own analyses they were diluted with water, boiled to a boiling point of

219–220° F., and filtered through double S. & S. No. 597 filters.¹ Their densities at 15° C. were then 1.325, 1.321 and 1.332, respectively. Two of these Vermont syrups gave lower conductivity values than any of the Canadian syrups, *viz.*, 110 and 115. The third gave a value of 122. The ash values of these three syrups were also exceptionally low. Complete data for these syrups, as obtained by Professor Jones and myself, are given in Table V.

TABLE V ANALYSES OF THREE VERMONT SYRUPS BY C. H. JONES AND BY J. F. SNELL

No.	Analyst	Per cent Total ash		Per cent Insoluble ash		Alkalinity Soluble ash		Conductivity value	Malic acid value
		Dry basis	Dry basis	Dry basis	Dry basis	ash	ash		
1	Jones	0.70	0.37	0.35			0.45		0.44
	Snell	0.71	0.59	0.37			0.44	115	
2	Jones	0.68	0.33	0.39			0.44		0.45
	Snell	0.83	0.32	0.42			0.50	122	
3	Jones	0.64	0.25	0.36			0.35		0.39
	Snell	0.70	0.23	0.37			0.38	110	

The minimum value yet found in a genuine syrup is 110. The maximum of 203 obtained with the syrup prepared in the iron kettle has not been reached in any other pure syrup. The highest value yet found in a syrup actually prepared for the market is 197. The limits of variation of genuine syrups may, therefore, be tentatively set at 110 to 200.

The mean conductivity of the 68 syrups may most fairly be estimated by giving the mean of the 22 syrups made from the trees on the Macdonald College farm a weight of 2—the same as one pair of early and late run syrups. We thus obtain for the 48 syrups—46 actual and 2 theoretical—a mean conductivity value of 150. This is approximately equal to the electrical conductivity of an 0.01 M aqueous solution of potassium chloride (141.2).

THE RELATION OF THE CONDUCTIVITY VALUE TO THE ASH DATA

Since the salt components of maple syrup are undoubtedly responsible for the electrical conductivity, relations between the conductivity value and the ash data are worthy of investigation. From the investigations of Hortvet,² Jones³ and Bryan⁴ it is clear that maple syrup ash consists largely (*viz.*, to the extent of about 85 per cent) of the carbonates of calcium and potassium, the two metals being present in about chemically equivalent quantities. The three investigators are in close agreement as regards the lime content which is in the neighborhood of 22 per cent. Bryan finds an average of 38 per cent of potash in 100 syrups, Jones one of nearly 35 per cent in 6 syrups, two of which were composites of a number of samples, while Hortvet finds about 31 per cent in each of two syrup ashes. Hortvet alone has determined carbonic acid. His results show an average of about 30 per cent in the two samples. The proportions of these three constituents of the ash may accordingly be placed at the following figures as a rough estimate:

¹ Jones, Vt. Agr. Expt. Sta., 18th Annual Report, 1905, 328; also Bulletin 167, 470 (1912).

² J. Am. Chem. Soc., 26, 1541 (1904).

³ Vt. Agr. Expt. Sta., 18th Annual Report, 1905, 331.

⁴ Bur. of Chem., U. S. Dept. Agr., Bulletin 134 (1910).

¹ Ostwald-Luther, *Physico-chemische Messungen*, 2nd edition, p. 407.

	Per cent Molecules	
K ₂ O ..	35	0.37
CaO ..	22	0.39
CO ₂ ..	30	0.68
Sum ..	87	

These results indicate that organic salts of potassium and calcium are the chief electrolytes of the syrup.¹ Potassium, having a higher ionic conductivity than calcium, may be expected to contribute a little more than an equal share to the conducting power of the

Considered by themselves, the ratios of Table VI would indicate that the closer relationships are those between, on the one hand, conductivity and *weight* of the *total* ash and on the other hand conductivity and *alkalinity* of *soluble* ash. It is to be remembered, however, that these syrups were all from the one bush, and were manufactured on a small scale in the laboratory. As will be pointed out later, they are also peculiar in their ratios of the alkalinities of soluble and insoluble ash. Table VII, which refers to more representative

TABLE VI RATIOS OF THE ANALYTICAL DATA FOR 22 SYRUPS MADE IN LABORATORY (SEE TABLE III)

	Number	A/B Conduc- tivity syrup ÷ Conduc- tivity ash	A/C Conduc- tivity syrup ÷ Total ash	A/D Conduc- tivity syrup ÷ Soluble ash	A/F Conduc- tivity syrup ÷ Alkalinity total ash	A/G Conduc- tivity syrup ÷ Alkalinity sol. ash	A/H Conduc- tivity syrup ÷ Alkalinity insol. ash	B/D Conduc- tivity ash ÷ Soluble ash	B/G Conduc- tivity ash ÷ Alkalinity sol. ash	E/G Alkal. total ash ÷ Alkal. sol. ash	G/H Alkal. sol. ash ÷ Alkal. insol. ash
Mixed sap of hard and soft maples	1		158	341	127	333	205			2.62	62
	2	2.52	166	248	115	328	178	92	122	2.84	54
	3	2.53	164	379	99	313	144	150	124	3.17	46
	4	2.73	161	268	108	333	178	98	122	3.09	53
	5	2.38	145	250	112	309	175	105	129	2.77	57
	6	2.33	153	229	113	293	185	98	126	2.59	63
	7	2.76	162	394	106	288	168	143	104	2.71	57
	8	2.24	167	292	137	338	230	131	151	2.47	68
	9	2.70	153		96	314	138		116	3.28	44
	10	2.48	125	277	101	331	145	112	133	3.28	44
	11	2.33	129	252	96	268	150	108	115	2.79	56
	12	2.67	142	337	96	316	138	126	118	3.29	44
Average mixed sap.....		2.52	152	297	109	314	170	116	124	2.91	0.54
Per cent deviation of maximum from mean.....		9.5	9.9	32.7	25.7	7.6	35.3	29.3	21.8	13.0	9.7
Per cent deviation of minimum from mean.....		11.1	17.8	22.9	11.9	14.6	18.8	20.7	16.1	15.1	29.2
Hard maple sap	13	3.02	167	354	124	354	191	117	117	2.85	54
	14	2.66	152	310	118	330	183	116	124	2.80	55
	15	2.70	143	311	105	292	164	115	108	2.78	56
	16	2.96	152	247	116	329	178	83	111	2.84	54
	17		141	308	95	285	144			2.98	50
	18	2.48	147	313	97	300	144	127	121	3.09	48
	19	2.63	146	361	111	326	169	137	124	2.69	52
Average hard maple.....		2.74	150	315	109	317	168	116	118	2.86	53
Per cent deviation of maximum from mean.....		10.2	11.3	14.6	13.8	11.7	13.7	18.1	5.1	8.0	5.7
Per cent deviation of minimum from mean.....		9.5	6.0	21.6	12.8	10.1	14.3	28.4	5.9	5.9	9.4
Soft maple sap	20	2.48	149	285	114	335	172	115	135	2.95	51
	21	2.33	167	321	123	307	205	138	132	2.50	67
	22		161	274	117	269	206			2.31	76
Average soft maple.....		2.41	159	293	118	304	194	127	134	2.59	65
Per cent deviation of maximum from mean.....		2.9	5.03	9.6	4.2	10.2	6.2	8.7	0.7	13.9	16.9
Per cent deviation of minimum from mean.....		3.3	6.3	6.5	3.4	11.5	11.3	9.4	1.4	10.4	21.5
General average ..		2.58	154	302	110	313	172	117	123	2.85	0.55
Maximum.....		3.02	167	394	137	354	230	150	151	3.29	76
Minimum.....		2.24	125	229	95	268	138	92	104	2.31	44
Per cent deviation of maximum from mean.....		17.1	8.4	30.5	24.5	13.1	33.7	28.2	22.8	15.4	26.7
Per cent deviation of minimum from mean.....		13.2	18.8	24.2	13.6	14.4	19.8	21.4	15.4	18.9	26.7

syrup. But its preponderance is not such as to justify a confident prediction that the conductivity value will be more closely related to the soluble ash (consisting mainly of potassium carbonate) or its alkalinity than to the total ash or its alkalinity.

I have, therefore, made calculations of the ratios of several of the data of Tables III and IV and present these ratios in Tables VI and VII.

¹ Magnesium and sodium salts are present in minor proportions.

samples, shows no material difference in the variability of the ratios of the conductivity value to the different ash data. If anything, the conductivity is more closely related to the total alkalinity than to the separate alkalinities of either the soluble or the insoluble ash. The range of variation of any of these ratios is somewhat wider than that of the ratios of the total alkalinity to the soluble alkalinity.

TABLE VII—RATIOS OF THE ANALYTICAL DATA FOR THE 12 QUEBEC SYRUPS OF TABLE IV

Number	A C Syrup Conductivity ÷ Total ash	A D Syrup Conductivity ÷ Soluble ash	A/E Syrup Conductivity ÷ Alkalinity ash	A/G Syrup Conductivity ÷ Alkalinity soluble ash	A H Syrup Conductivity ÷ Alkalinity ash	F G Alkal. total ash ÷ Alkal. sol. ash	G H Alkal. sol. ash ÷ Alkal. insol. ash
1	166	289	128	289	229	2.26	79
2	182	253	148	257	347	1.74	135
3	171	249	145	287	292	1.98	102
4	162	228	149	290	309	1.94	107
5	188	294	165	327	334	1.98	102
6	163	250	134	259	279	1.93	108
7	128	228	135	273	267	2.02	98
8	142	205	135	253	289	1.88	114
9	136	201	115	205	260	1.79	126
10	173	262	133	266	266	2.00	100
11	155	230	137	276	271	2.02	98
12	139	255	138	293	263	2.11	90
Average.....	159	245	139	273	284	197	105
Per cent deviation of max. from mean	18.2	18.0	18.7	19.8	22.2	14.7	28.6
Per cent deviation of min. from mean	19.5	18.0	17.2	24.9	19.4	11.7	24.8

CONDUCTIVITY VALUE OF THE ASH

Among the data of Tables III and VI is included for 19 syrups a figure designated "Conductivity Value of the Ash." This was determined according to the following method: 5 grams of syrup are ashed in a platinum dish. The ash is boiled with 30 cc. water for two minutes, filtered through a 7 cm. filter and washed with hot water to a volume of nearly 50 cc. (the residue is ignited and weighed as the insoluble ash). The cooled filtrate is made up to exactly 50 cc. and the conductivity measured at 25° C. The solution is washed out of the conductivity cell and titrated for alkalinity of soluble ash.

This method departs from the conventional one for determination of soluble and insoluble ash in maple products in using only 50 cc. of hot water on the ash of 5 grams of syrup, instead of 100 cc. Possibly it might be preferable to adhere to the conventional method of separating soluble and insoluble ash and to make the determination of conductivity value of ash in a volume of 100 cc. instead of 50 cc.

To determine whether there is any material difference between the results obtained with the two different quantities of wash water, Mr. Scott has repeated the determinations upon syrups Nos. 2, 5 and 11, using 100 cc. of wash water. The results obtained by the two methods are compared below:

		Alkalinities as determined with use of					
		50 cc. wash water			100 cc. wash water		
Syrup	Date made	Sol. ash	Insol. ash	Ratio	Sol. ash	Insol. ash	Ratio
2	Apr. 7-9	50	92	0.54	46	82	0.56
5	Apr. 12	47	83	0.57	52	86	0.60
11	Apr. 25	47	84	0.56	52	84	0.62
Average,				0.56	0.59		

I infer from these results that the difference between the two methods of washing is of little consequence.

¹ In the A. O. A. C. provisional method for saccharine products in general, only 60 cc. of water are used. See Bur. of Chem., *Bulletin* 107, 68 (1908). Hortvet followed this method.

As intimated above, the syrups upon which the determination of the conductivity of the ash was made are peculiar in their low ratio of alkalinity of soluble to that of insoluble ash. They average 0.54. On the 94 syrups examined by Jones, the average value of this ratio is 0.94; on the 13 upon which Hortvet made these determinations it is 0.85; Bryan's general average for 481 syrups is 0.77, although for the 100 syrups selected by him for ash analysis, I find the average to be 0.87; and the average for the 12 syrups of Tables IV and VII of the present paper is 1.05. It is clear, therefore, that the syrups made in the laboratory (Tables III and VI) are of exceptional character. Under these conditions I do not feel justified in drawing any conclusions from the results obtained in the determination of the electrical conductivity of the ash solution. This property is, however, worthy of further study.

TABLE VIII—CONDUCTIVITY VALUES OF NON-MAPLE SYRUPS

Number	Description	Specific gravity	Conductivity value
1	Corn syrup	1.40	2.51
2	Golden syrup	1.44	414
3	Molasses	...	656
SYRUPS DILUTED TO DENSITY OF MAPLE SYRUP			
No. 1 diluted	Corn syrup	1.339	253
4	Corn syrup	1.320	359
5	Corn syrup	1.320	209
No. 2 diluted	Golden syrup	1.320	427
6	Golden syrup	1.320	392
7	Golden syrup	1.320	403
8	Molasses	1.320	1121
9	Molasses	1.320	1280
10	Molasses	1.320	604
11	Molasses	1.320	1250
12	Cane sugar syrup from granulated sugar	1.314	0.5
13	Cane sugar syrup from pale brown sugar	1.329	178
14	Cane sugar syrup from pale brown sugar	1.333	185

THE CONDUCTIVITY VALUES OF NON-MAPLE SYRUPS

Table VIII gives the conductivity values of a number of non-maple syrups. It will be seen that syrup made from granulated sugar is practically a non-conductor, that syrups from partially refined cane sugar may give values within the limits found for pure maple syrups, and that all of the others give conductivity values distinctly above the limits for maple. It is clear, therefore, that values either above or below the limits for genuine maple syrup may be produced by adulteration. Syrups yielding values either abnormally high or abnormally low may be condemned without further examination. But it is clear that the possession of a normal conductivity value is not in itself adequate evidence of the purity of a syrup.

USEFULNESS OF THE METHOD

In Table IX are given the results of analysis of 34 syrups as found upon the market in the Provinces of Saskatchewan, Alberta and British Columbia in 1911 and 1912. The modified Winton lead number was determined upon the quantity of syrup containing 25 grams of dry matter.

It will be seen that the conductivity method would condemn 15 of these samples, and that every one of

TABLE IX—SYRUPS PURCHASED IN THE CANADIAN WEST

Number	Sold as	Specific gravity	Per cent Moisture	Per cent Total ash Dry basis	Per cent Insoluble ash Dry basis	Alkalinity soluble ash	Modified Winton		Conductivity value
							Alkalinity insoluble ash	Lead Number (Dry basis)	
1	Pure	1.309	36.8	0.13	0.03	0.11	0.11	0.46	23
2	Pure	1.337	32.2	0.09	0.05	0.06	0.13	0.10	24
3	Pure	1.304	37.6	0.67	0.29	0.34	0.46	1.15	113
4	Pure	1.315	35.8	0.62	0.31	0.34	0.52	1.37	114
5	Pure	1.332	33.0	0.76	0.34	0.47	0.60	1.99	134
6	Pure	1.315	35.8	0.95	0.50	0.42	0.58	2.38	150
7	Pure	1.323	34.4	0.84	0.44	0.46	0.70	1.96	143
8	Pure	1.318	35.3	0.91	0.43	0.42	0.74	2.09	159
9	Pure	1.326	34.0	0.41	0.20	0.23	0.38	0.80	79
10	Pure	1.332	33.0	0.82	0.42	0.50	0.66	1.92	133
11	Pure	1.316	35.6	0.07	0.04	0.08	0.10	0.23	21
12	Pure	1.326	34.0	0.85	0.30	0.38	0.42	1.40	123
13	Pure	1.344	31.1	0.64	0.18	0.28	0.28	0.99	90
14	Pure	1.352	29.8	0.72	0.30	0.35	0.45	1.61	117
15	Pure	1.340	31.7	0.93	0.33	0.48	0.50	1.58	142
16	Pure	1.323	34.5	0.93	0.38	0.49	0.61	2.06	152
17	Pure	1.330	33.4	0.33	0.14	0.20	0.26	0.84	60
18	Pure	1.335	32.5	0.43	0.19	0.23	0.32	0.83	66
19	Pure	1.315	35.8	0.50	0.22	0.29	0.38	1.09	85
20	Pure	1.320	35.0	1.09	0.40	0.50	0.72	2.25	160
21	Pure	1.333	32.9	0.70	0.33	0.38	0.58	1.68	128
22	Pure	1.327	33.8	0.74	0.21	0.31	0.46	1.33	93
23	Pure	1.331	33.2	0.54	0.28	0.32	0.42	1.41	97
24	Pure	1.340	31.7	0.59	0.23	0.30	0.46	1.29	94
25	Pure	1.324	34.3	1.22	0.43	0.49	0.72	2.33	145
26	Pure	1.325	34.2	0.93	0.52	0.47	0.83	2.56	149
27	Pure	1.326	34.0	0.85	0.33	0.50	0.57	2.11	146
28	Pure	1.329	33.5	0.62	0.21	0.32	0.48	1.26	94
29	Pure	1.335	32.5	0.65	0.25	0.40	0.57	1.36	113
30	Pure	1.329	33.5	0.35	0.15	0.16	0.33	0.86	64
31	Compound	1.337	32.2	0.10	0.04	0.09	0.09	0.20	24
32	Compound	1.351	30.0	0.56	0.14	0.31	0.23	0.72	136
33	Maple flavor	1.351	30.0	0.21	0.13	0.15	0.17	0.47	48
34	Maple flavor	1.339	31.9	0.30	0.25	0.36	0.42	1.68	129

Standards of purity:

Canada.....	35.0	0.60	0.12	..	1.20
Vermont.....		0.77	0.23	..	

Ordinary limits for genuine syrup:

Minimum.....		0.75	0.23	0.30	0.36	110
Maximum.....		1.35	0.80	0.66	0.94	200

these 15 is also condemned by a complete analysis. Syrups 32 and 34, however, which would pass the conductivity test, are condemned by the other determinations, and Nos. 3, 4 and 29, which are near the limit in conductivity value and which, being of the same brand as Nos. 9, 19, 21, 22, 24 and 28, are probably adulterated, are also near the limits of the Canadian standard in respect to the other analytical data and are below the Vermont standard on total ash. When one considers that all the ordinary analytical work on the 15 samples might be omitted, the usefulness of the conductivity method is apparent.

SUMMARY

1. A rapid method of detecting adulteration of maple syrup with commercially pure sucrose is described.

2. The "conductivity value" is defined as 100,000 times the specific conductivity at 25° C. of a mixture of one volume of syrup with two volumes of water.

3. The limits of conductivity value for pure maple syrup are tentatively set at 110 to 200.

4. The relation of conductivity value to ash data is discussed.

5. The usefulness of the test is illustrated.

THE COMPOSITION OF DIFFERENT VARIETIES OF RED PEPPERS¹

By L. M. TOLMAN AND L. C. MITCHELL

Received May 26, 1913

CAYENNE OR CHILLI

General Description.—Cayenne or chilli is a small fruited pepper, a variety of *Capsicum frutescens* L., a species of *Capsicum*, which is a genus of the family *Solanaceae*, indigenous to the American tropics, but now grown or cultivated in nearly all tropic and subtropical countries. It is characterized by its extreme pungency and the small size of the pods. The leading commercial varieties (1911) are African and Japanese.

The African cayenne or chillies come chiefly from the ports of Mombasa and Zanzibar, British East Africa, and are usually designated in the trade by the name of the port from which shipped; they are from 10 to 15 mm. in length, dark, dull red in color, and extremely pungent; they are ground for use. A few of the samples contained some unattached stems and calyxes.

The Japanese chillies come from the port of Kobe, Japan; these are from 15 to 40 mm. in length, bright red in color, clean, containing very few stems or calyxes, and are used chiefly in the underground condition for the preparation of the so-called "chilli sauce."

Cayenne or chilli contains a fixed, bland oil, found

¹ Authors' abstract of *Bull.* 163, Bureau of Chem., Dept. of Agr.

in both pods and seeds, but more abundantly in the latter, considerable resinous and mucilaginous material, a red coloring matter confined to the shell, and the active principle, capsaicin, to which the pungency is due. The capsaicin is present in both

Analyses.—In addition to the African and Japanese varieties which make up the major portion of the importations, two other apparently different varieties were examined. N. Y. 25482 is a nearly round cayenne or chilli from India, 15 to 25 mm. in length and 10 to

TABLE I—RESULTS OF ANALYSES OF CHILLIES, OR CAYENNE PEPPERS

Serial No.	Original					Sifted				
	Total ash	Ash insoluble in 10 per cent hydrochloric acid	Sand-free ash	Volatile ether extract	Non-volatile ether extract	Total ash	Ash insoluble in 10 per cent hydrochloric acid	Sand-free ash	Volatile ether extract	Non-volatile ether extract
Per cent										
African (Mombasa) chillies or cayenne:										
N. Y. 24584....	6.45	1.56	4.89		17.91	5.98	0.82	5.16		18.34
N. Y. 24605....	5.34	0.44	4.90		18.59	5.51	0.46	5.05		18.45
N. Y. 24606....	7.38	1.73	5.65		17.70	5.71	0.72	4.99		18.60
N. Y. 24610....	7.44	1.03	6.41		19.00	6.16	0.72	5.44		18.46
N. Y. 24701....	4.88	0.45	4.43	0.24	19.36	4.80	0.52	4.28	0.28	19.02
N. Y. 24802....	7.72	2.59	5.13	0.41	16.43	5.80	0.72	5.08	0.47	16.41
N. Y. 24803....						5.51	0.52	4.99	0.74	17.03
N. Y. 24855....	5.81	1.00	4.81	1.21	18.60	5.71	0.64	5.07	0.85	18.63
N. Y. 24885....	5.48	0.55	4.93	0.89	18.60	5.18	0.44	4.74	1.11	18.14
N. Y. 25027....	5.51	0.78	4.73	0.51	16.81	5.13	0.50	4.63	0.49	17.28
N. Y. 25028....	6.96	1.63	5.33	0.49	15.88	5.64	0.74	4.90	0.56	16.87
N. Y. 25029....	5.83	0.76	5.07	0.73	16.21	5.59	0.65	4.94	0.65	16.59
N. Y. 25031....	7.45	2.25	5.20	0.52	17.93	5.86	0.85	5.01	0.26	17.33
N. Y. 25190....	5.94	0.93	5.01	0.65	16.09	5.56	0.77	4.79	0.44	16.82
N. Y. 25195....	5.72	0.65	5.07	0.54	15.90	5.31	0.50	4.81	0.58	16.07
N. Y. 25245....	5.64	0.86	4.78	0.74	17.95	5.33	0.66	4.67	0.75	17.40
N. Y. 25348....	5.76	0.73	5.03	0.75	16.22	5.19	0.54	4.65	0.72	16.53
N. Y. 25399....	5.53	0.73	4.80	1.09	17.14	5.38	0.59	4.79	0.74	17.83
N. Y. 25470....	7.07	1.95	5.12	1.59	16.52	5.75	0.59	5.16	0.63	17.41
N. Y. 25481....	6.21	1.19	5.02	1.72	15.91	5.66	0.74	4.92	1.37	16.40
N. Y. 25566....	8.41	3.03	5.38	0.73	16.00	5.55	0.62	4.93	0.76	17.01
N. Y. 25634....	5.35	0.50	4.85	0.28	16.89	4.86	0.37	4.49	0.25	16.81
I. S. 3817-C....	6.66	1.42	5.24	1.15	17.60	5.24	0.55	4.69	0.71	19.68
I. S. 3819-C....	5.77	0.87	4.90	0.97	18.76	5.58	0.73	4.85	0.40	18.38
I. S. 3820-C....	6.18	1.09	5.09	0.91	16.99	5.38	0.55	4.83	0.66	18.13
I. S. 3822-C....	17.62(a)	11.38(a)	6.24(a)	0.76(a)	14.73(a)	5.74	0.72	5.02	0.50	18.34
I. S. 3823-C....	7.31	2.26	5.05	0.96	16.65	5.73	0.73	5.00	0.82	16.65
Average....	6.31	1.24	5.07	0.81	17.26	5.51	0.63	4.88	0.64	17.52
Maximum....	8.41	3.03	6.41	1.72	19.00	6.16	0.85	5.44	1.37	19.68
Minimum....	5.34	0.44	4.73	0.28	15.88	4.86	0.37	4.49	0.25	16.07
Japanese (Kobe) chillies or cayenne:										
N. Y. 24819....	5.08	0.38	4.70	1.59	20.41	5.06	0.38	4.68	0.34	19.54
N. Y. 25004....	5.21	0.58	4.63	0.32	19.04	5.44	0.49	4.95	0.25	20.00
N. Y. 25010....	5.69	0.53	5.16	0.35	20.51	5.08	0.48	4.60	0.32	18.15
N. Y. 25011....	5.41	0.77	4.64	0.29	18.08	5.12	0.51	4.61	0.22	17.67
N. Y. 25012....	5.18	0.66	4.52	0.20	18.39	5.34	0.46	4.88	0.20	19.09
N. Y. 25013....	5.76	0.73	5.03	0.19	20.17	5.70	0.51	5.19	0.25	20.57
N. Y. 25014....	6.20	1.07	5.13	0.28	20.26	5.19	0.53	5.26	0.97	22.89
N. Y. 25026....	5.86	0.57	5.29	0.88	23.21	5.10	0.30	4.80	0.10	20.14
N. Y. 25398....	5.26	0.41	4.85	0.24	20.77	5.34	0.32	5.02	0.88	18.88
N. Y. 25408....	5.55	0.41	5.14	1.01	18.51	5.50	0.27	5.23	0.96	20.73
N. Y. 25409....	5.45	0.31	5.14	0.72	21.11	5.26	0.33	4.93	0.60	20.39
N. Y. 25410....	5.41	0.33	5.08	0.75	20.68	5.15	0.37	4.78	0.05	19.21
N. Y. 25567....	5.32	0.57	4.75	0.09	19.43	5.36	0.39	4.97	0.20	17.81
N. Y. 25678....	5.40	0.36	5.04	0.59	17.10	5.40	0.47	4.93	0.20	19.10
N. Y. 25679-A....	5.52	0.54	4.98	0.27	20.14	5.82	0.47	5.35	0.25	20.01
N. Y. 25679-B....	5.90	0.40	5.50	0.40	19.44	5.40	0.37	5.03	1.14	21.20
I. S. 3818-C....	5.71	0.44	5.27	1.39	21.69	5.37	0.42	4.95	0.43	19.71
Average....	5.52	0.53	4.99	0.56	19.94	5.82	0.53	5.35	1.14	22.89
Maximum....	6.20	1.07	5.50	1.59	23.21	5.06	0.27	4.60	0.05	17.67
Minimum....	5.08	0.31	4.52	0.09	17.10					
Cherry:										
N. Y. 25482....	6.62	1.23	5.39	1.18	16.17	5.82	0.51	5.31	0.77	17.56
Sweet, red pepper:										
B. 4484....	6.04	0.40	5.64	0.72	12.80	5.93	0.42	5.51	0.75	13.64
Siftings:										
I. S. 3821-C....	62.63	51.53								

(a) Not included in average, maximum, and minimum.

the seeds and the shell, but the larger part is found in the placenta. The red coloring matter is soluble in ether, petroleum ether, carbon bisulfide, and chloroform, but very slightly soluble in alcohol.

15 mm. in width, belonging to *C. frutescens baccatum* L., and known to the trade under the name "cherry." The color of the pods varies from dark red to a brownish yellow; the sample was clean and had no

stems or calyxes. B. 4484 is a capsicum from Japan and is from 45 to 65 mm. in length, bright red in color, clean, and had the stems and calyxes attached to the pods. Analysis indicates this to be a sweet, red pepper.

In order to determine the characteristic taste and flavor and to find out definitely what part or parts of the pod contained the capsaicin, pods from different samples were broken up into the following parts: shells, seeds, and placentae. The shells from the Japanese chillies have a slightly bitter, slightly acid, bland taste (similar to that of pimenton) and are mildly pungent; the seeds, a sweetish, bland, mildly pungent taste; and the placentae extremely pungent, containing nearly all the active principle, capsaicin; the ground product has a very pungent taste. The shells from the African chillies have a slightly acid, pungent taste; the seeds, a sweetish, bland, pungent taste; and the placentae, extremely pungent; the ground product has a very pungent taste.

The samples were taken from the various imports as they were received by the regular United States Treasury samplers by means of coffee triers which were inserted into the packages or bales and the samples allowed to flow out into paper bags.

In each instance an analysis was made of the original and of the part which has been carefully sifted with an ordinary coarse 3 mm. hand sieve to remove as much sand as possible. The two analyses are placed on the same line, so that a ready comparison may be made.

The African or Mombasa chillies have the appearance of being dirty or sandy, and the analyses plainly show this condition. They are said to grow wild in the interior of tropical East Africa and are gathered by semicivilized people. They are dried on the ground and roofs of the huts or houses, thus subjected to the various conditions of the weather. They contain dirt, sand, stems, etc., and necessarily need cleaning before being ground for use. Attention is called to one sample, I. S. 3822-C, showing a most remarkable amount of sand and dirt present, which apparently could readily be sifted out, as the analysis of the sifted product shows a normal condition. The results on the sifted portions are remarkably uniform, showing only slight variations between the maximum and the minimum.

The Japanese or Kobe chillies differ in appearance, being very clean-looking and of a much brighter color. The results plainly show this difference, as the amounts of sand and ash are materially lower. Many samples contained less than one-half per cent. of sand, while in the Mombasa chillies practically none of the 50 samples ran as low as that.

I. S. 3822-C is so abnormal in its ash and ash insoluble in acid that none of the results are included in the average, maximum and minimum results. Note how the sifting reduces the mineral matter and increases the nonvolatile ether extract and crude fiber, making them normal.

PAPRIKA

General Description.—Paprika is a large-fruited

pepper, grown in Hungary, a variety of *Capsicum annuum* L., a species of *Capsicum*, which is a genus of the family *Solanaceae*. When powdered, it has a deep red color and a sweetish, mildly pungent flavor. Its origin is somewhat obscure, but it apparently originated in America, whence it can be traced from Spain, through Greece and Turkey, to Hungary. It has been variously designated as Turkish pepper or paprika, Hungarian pepper or paprika, or garden pepper.

According to Csonka and Varadi,¹ there are five grades of Hungarian paprika known to commerce, as follows:

Rosenpaprika or Rózsapaprika.

Königspaprika or Királypaprika.

Merkantilpaprika.

Kranzpaprika.

Geschnittener Paprika.

The two last grades are practically unknown in the United States, as all of the paprika coming into the United States is ground.

Rosenpaprika, or Rózsapaprika, is the best grade of paprika made in Hungary, and has been known under this name since 1860, obtaining its name from its beautiful red color. It is produced with the utmost care from special, selected pods, the spotted and damaged parts being cut out, the placentae, the stalks, and the stems removed, and the seeds and shells washed many times before being ground. The ground product has a bright red color and is distinguished by its pleasant taste. It will be noted that even in the highest grade of paprika the seeds are ground with the shells.

The second grade, or Königspaprika, is prepared by grinding the whole pod without selecting any of the pods, and includes not only the seeds, but also the stems, in the amount naturally occurring with the pod.

The Mercantile grade is produced from the spotted pods remaining from the selection for the finer grades and from the pods containing flaws, the lower grades of the Mercantile being ground with the stalks, stems, and other waste parts. This grade has, as a rule, a much more pungent taste and has a pale yellow color.

Szigeti² classes paprika in four grades, making a special grade above the Rózsapaprika, which he calls Ectes paprika; otherwise, he classifies them in practically the same manner as the previous authors. He calls attention to the fact that the Mercantile grade consists of scraps and waste from the other grades, and that the product is more pungent and has a yellow color, as distinguished from the higher grades.

Analyses.—The samples which were examined by the authors, the results of which are given in Table III, were received under the seal of the Royal Hungarian Ministry of Agriculture through the Department of State. They consisted of large wreaths, were of a bright red color, sound, from 6 to 10 cm. in length and from 2.5 to 4.0 cm. in diameter, and of a conical shape.

¹ *Der Szegeder Paprika und der Szegeder Paprikahandel*, 1907.

² *Zts. Landw. Versuchsw. Oesterr.*, 5, 1208-22 (1902).

In order to get at the composition of the different parts of the paprika, each sample was subdivided into five different portions, as follows: *First*, ground shells, stems, seeds and placentae; *second*, ground shells, seeds, and placentae; *third*, ground shells alone; *fourth*, ground seeds and placentae alone; *fifth*, ground stems alone. In the preparation of these products, they were ground separately and passed through a 0.5 mm. sieve, with the exception of the seeds, which were passed through a 1 mm. sieve.

The results of this separation in percentage of shells, seeds and placentae, and stems, are as follows:

TABLE II—SEPARATION OF HUNGARIAN PAPRIKAS FOR ANALYSIS

(21 samples)	Shells Per cent	Seeds and placentae Per cent	Stems Per cent
Average.....	56.4	36.1	7.5
Maximum.....	63.7	43.2	9.4
Minimum.....	50.5	28.1	6.0

The percentage was determined so that the effect of the addition of any of the parts in excess of the normal might be calculated, and thus a check had on the actual determinations made on the various grindings.

The percentage of these various parts is also of value in the microscopic examination of the ground product, in order to determine whether or not there is an abnormal percentage of seeds or stems present. It will be seen from this table that the percentage of stems never exceeds 10 per cent.

Table III contains the results obtained by the authors on the various samples of Hungarian paprika, separated into their various parts and ground.

TABLE III—ANALYTICAL RESULTS ON GROUND HUNGARIAN PAPRIKA

Serial No.	Volatilité at 70° C. in <i>vacuo</i> Per cent	Total ash Per cent	Ash insoluble in 10 per cent hydrochloric acid Per cent	Sand-free ash Per cent	Total ether extract Per cent	Non-volatile ether extract Per cent	Volatilité ether extract Per cent	Crude fiber Per cent	Seeker's method		Index of refraction at 40° C.
Shells, seeds and placentae, and stems:									Non-volatile ether extract Per cent	Iodine number	
Average.....	3.47	5.63	0.28	5.36	14.49	14.04	0.42	21.93	12.61	132.6	1.4806
Maximum.....	3.76	6.03	0.33	5.73	16.56	16.43	0.89	22.76	15.00	134.0	1.4854
Minimum.....	3.29	5.08	0.24	4.82	12.87	12.21	0.08	20.69	10.86	129.8	1.4758
Shells, seeds and placentae:											
Average.....	3.51	5.22	0.26	4.96	15.62	15.28	0.34	21.56	13.91	131.9	1.4799
Maximum.....	4.16	5.56	0.31	5.25	17.43	17.35	0.90	23.18	15.08	133.2	1.4834
Minimum.....	3.11	4.66	0.20	4.41	14.50	13.94	0.07	20.47	12.64	129.0	1.4756
Shells:											
Average.....	3.63	6.60	0.28	6.33	6.34	6.07	0.28	23.19	4.68	140.1	(a) } 7 samples
Maximum.....	4.00	7.11	0.37	6.84	7.19	6.90	0.44	24.07	5.26	149.5	(a) }
Minimum.....	3.44	6.29	0.22	6.04	5.38	5.14	0.16	22.20	4.14	133.2	..
Seeds and placentae:											
Average.....	3.97	3.63	0.26	3.38	27.02	26.96	0.06	20.76	23.53	133.5	1.4696
Maximum.....	4.23	3.80	0.30	3.59	27.71	27.56	0.15	21.60	24.96	134.0	1.4699
Minimum.....	3.73	3.38	0.21	3.13	25.99	25.97	0.00	20.89	22.53	133.1	1.4691
Stems:											
Average.....	5.22	10.59	0.85	9.74	2.77	2.54	0.23	30.67
Maximum.....	5.78	11.35	1.20	10.67	3.40	3.05	0.35	32.86
Minimum.....	4.66	9.84	0.66	9.18	2.25	2.11	0.15	29.34

(a) Not read.

PIMENTON, OR PIMIENTO¹

General Description.—The pimenton, or pimiento, is a large-fruited pepper, a variety of *Capsicum annuum* L., grown in Spain, and, under the standard

¹ "Pimenton" should not be confused with "pimento" or "pimenta" which are applied to Jamaica pepper or allspice. "Pimenton" is the definite term used to designate the Spanish product when ground. The usual term in the trade is Spanish paprika.

given in Circular 19, Office of the Secretary, would be classified, when ground, as paprika. The succulent pericarp of this pepper is much used for stuffing of olives, while the dried pod is ground as a spice. A large quantity of this pepper imported to the United States is used largely on account of its high coloring properties. The taste and flavor are quite different from the Hungarian paprika.

The samples which were examined during this study were received under seal from the American consul-general at Barcelona, Spain, and consisted of large wreaths, the pods of which were of a bright red color, sound, and from 2.5 to 4 cm. in length, and from 4 cm. to 6 cm. in diameter, having a nearly round shape.

Analyses.—Five different grindings were made from each set of peppers. In the *first* case, the shells, seeds and placentae, and stems, were ground together; in the *second*, the shells, seeds and placentae; in the *third*, the shells alone; in the *fourth*, the shells and placentae; in the *fifth*, the stems alone. Table IV gives the percentage composition of the various parts of the pods used in the above ground samples:

TABLE IV—SEPARATION OF SPANISH PIMENTON FOR ANALYSIS

Serial No. (18 samples)	Shells Per cent	Seeds and placentae Per cent	Stems Per cent
Average.....	55.3	36.0	8.7
Maximum.....	58.1	37.4	10.9
Minimum.....	53.1	34.9	6.0

The percentage was determined so that the effect of an addition of any of the parts in excess of the normal might be calculated and thus a check had on the actual determinations made on the various grindings. The percentage of these parts is also of value in the

microscopical examination of the ground product in order to determine whether or not there is an abnormal percentage of any of the parts.

Table V gives the analytical results on the various ground samples.

CONCLUSIONS

Cayenne.—The first point of special interest to be

TABLE V.—ANALYTICAL RESULTS ON GROUND SPANISH PIMENTON, OR PIMENTO

Serial No.	Volatiles at 70° C. in <i>vacuo</i> Per cent	Total ash Per cent	Ash insoluble in 10 per cent hydrochloric acid Per cent	Sand-free ash Per cent	Total ether extract Per cent	Non-volatile ether extract Per cent	Volatiles ether extract Per cent	Crude fiber Per cent	Seeker's method			Index of refraction at 40° C.
									Non-volatile ether extract Per cent	Iodine number		
Shells, seeds and placenta, and stems:												
Average	5.06	7.39	0.35	7.04	12.34	11.87	0.47	20.13	10.34	136.7	1.4805	7 samples
Maximum	5.98	7.86	0.48	7.54	13.06	12.58	0.69	20.59	10.81	137.3	1.4818	
Minimum	4.31	6.98	0.29	6.69	11.93	11.30	0.10	19.53	9.81	136.0	1.4776	
Shells, seeds and placenta:												
Average	4.83	6.98	0.32	6.66	12.91	12.47	0.44	19.49	10.67	136.1	1.4801	8 samples
Maximum	5.09	7.35	0.40	6.98	13.85	13.34	0.60	20.34	11.30	137.2	1.4810	
Minimum	4.52	6.60	0.24	6.26	11.83	11.58	0.25	18.76	9.80	134.5	1.4792	
Shells:												
Average	4.83	7.99	0.32	7.67	7.02	6.30	0.71	18.04	4.46	141.0	1.4963	8 samples
Maximum	5.02	8.46	0.37	8.09	7.52	6.81	1.05	18.70	4.67	143.7	1.4968	
Minimum	4.74	7.55	0.26	7.29	5.85	5.44	0.41	17.26	4.26	136.7	1.4958	
Seeds and placenta:												
Average	3.92	4.79	0.27	4.52	23.32	23.10	0.21	22.37	19.99	129.9	1.4699	8 samples
Maximum	4.12	5.02	0.31	4.76	24.89	24.58	0.42	24.08	21.35	130.8	1.4702	
Minimum	3.59	4.43	0.22	4.12	22.15	21.82	0.05	19.90	19.11	128.1	1.4695	
Stems:												
Average	5.35	14.53	0.73	13.81	1.76	1.44	0.31	29.43	8 samples
Maximum	5.98	15.77	1.07	14.91	2.45	2.05	0.49	30.98	
Minimum	4.86	13.00	0.58	12.36	1.48	1.22	0.15	27.66	

noted is the fact that the Mombasa, or African, chillies now coming into this country are exceedingly dirty, and must necessarily be very carefully cleaned before they are ground. This condition is undoubtedly brought about by the fact that they grow wild in the interior of Africa, and are gathered by semi-savage tribes and dried under various conditions.

It is also likely that the conditions which control the production of this product may vary in the course of a number of years, so that the cayenne on the market may vary from time to time as the source of the chillies varies.

At the present time, a considerable amount of small, round-shaped chillies, known as "cherries," grown in India, is being brought into this country, and practically none of the true Zanzibar chillies is being received, although some chillies are still shipped from Zanzibar which are undoubtedly the same as those coming from Mombasa, and their source is the interior of Africa and not the island of Zanzibar.

The sand present in these products appears to be entirely of an extraneous nature, and they can be sifted so that an entirely uniform product is obtained. An examination of the tables shows that the sand-free ash of these products, regardless of source, is extremely uniform, and as a criterion of the product it would appear that this figure would be of great value.

The Kobe, or Japanese, chillies are comparatively clean and need but little sifting to produce a satisfactory product. These, however, are used in the preparation of "chilli sauce," and not for grinding purposes.

A careful study of the various tables shows that in judging the various varieties of cayenne—African, Japanese, and Indian—they should be compared with data obtained upon chillies from the same source.

Hungarian Paprika.—From a study of the literature and the information available in the course of this investigation, it would appear that the word "paprika" has generally referred in the past to a product made in Hungary, but now it is applied to similar products produced in Spain and America; it is clear that the

terms "Rosenpaprika" and "Rózsapaprika" are limited to a well-defined product which has been made in Hungary for a long period of time and consists of the highest grade of pods ground without the stems.

Further, it is clear that the grinding of the stems with a product of this kind is simply for the purpose of producing more weight and acting as a filler, and that it does not add any valuable qualities to the product, as it contains no flavoring principles. It is also clear that the grinding of the seeds and placenta with the pods produces an improved product, and all of the facts seem to indicate that it is a well recognized and legitimate process.

The results show that paprika must be judged from data obtained upon samples of paprika from a known source.

Pimenton, or Spanish Paprika.—It appears from this investigation that this product is commonly known as "Spanish paprika," or "pimenton." It is quite different in its flavoring qualities and value from Hungarian paprika, and should be properly distinguished from it. It has very little pungency and its flavor is different from that of the Hungarian product.

Further, the analytical results upon the pimenton show that the different conditions under which it is grown have affected, to a greater or less extent, the amount of ash and other ingredients present, clearly showing that in the judging of these products it is necessary to compare the Hungarian paprikas with data upon Hungarian paprikas, and the Spanish pimentons with data upon Spanish pimentons.

It is shown that it is possible to distinguish by analytical methods and by characteristic properties, such as taste and odor, between the Hungarian paprikas and the Spanish pimentons. They have different uses, the pimenton being largely used for its coloring value, rather than for its flavor.

SOME DISTINCTIONS BETWEEN PEPSIN AND PEPTASE¹

By DR. R. WAHL

The far-reaching influence of peptonizing ferments in the brewing industry on the stability of the product, together with the fact that very little has been published on the nature and properties of the vegetable ferment, has led me to investigate the peptase of barley malt. Although I shall not attempt to go into experimental details and data to-day, the time being short and some of our experiments being still incomplete, I will state in a general way only some of the differences between pepsin and peptase, which have become apparent in the course of my work.

One of the chief differences between these two is that while pepsin (the proteolytic ferment derived from the animal organism) is comparatively easy to obtain in a dry form approximating purity, the same does not hold true of the vegetable peptase. So far, to my knowledge, the peptase has not been isolated, and our own experiments dealing with the obtaining of dry, stable, peptic preparations of vegetable origin have not been very successful. Although I have devised a process which enables me to produce malt extracts of high peptic strength, as outlined in my communication to the Eighth International Congress of Applied Chemistry, September, 1912, which has proven of great practical value to the brewing industry, all attempts to reduce the extract to a dry form without the sacrifice of the greater part of the peptic strength, have failed.

Another interesting difference is that while pepsin acts best in the presence of mineral acid—preferably hydrochloric—the peptonizing power of the peptase of malt is greatly enhanced by the presence of lactic acid, preferably of a bacterial nature. It seems evident that the peptic enzyme contained in malt is locked up (combined with some base, presumably of albuminous nature) and becomes active through liberation by bacterial acidity. The digestive power must be generated, as it were, and I find that bacterial lactic acid is the specific activator, having tried a large number of other acids, both mineral and organic, but with comparatively little effect. The remarkable fact is that the lactic acid necessary to activate the peptase is provided during the growth of the malt, having been introduced into the steeping water with the barley. The secretion in the animal organism of pepsin and its specific activator, hydrochloric acid, which has even led some authors to the belief that active pepsin is not pepsin in the free state, but a compound of pepsin with hydrochloric acid, is thus seen to offer quite a close parallel.

The optimum temperatures of these two proteolytic ferments, that is, the temperature at which the proteolytic action proceeds most favorably, also differ. While this temperature lies in the vicinity of 50° C. in the case of pepsin, I have found the most favorable temperature for the most thorough digestive action of the peptase to be as low as 35–40° C. Again, peptase in solution is rapidly destroyed at 60° C.

while pepsin is not. Furthermore, the peptase of the barley grain is capable of inverting albumen at the low temperature of say 2° C. while the proteolytic action of the pepsin at that temperature is practically nil. All of the heat-coagulable albumen contained in a cold water malt extract will be completely peptonized, which means, converted into the non-coagulable form, by permitting this extract to stand for a few days at this temperature, *viz.*, 2° C.

Finally, most of the customary tests employed in physiological chemistry to measure the proteolytic activity of gastric and similar juices, give no satisfactory results when applied to the peptase of barley grain. I have reference to such methods as those devised by Jacoby, Volhard, etc., and the well-known fibrin digestion test. So far the gelatin test depending upon the liquefaction of gelatine by proteolytic ferments, suggested by Schidrowitz, and which I have slightly modified, has proven the one most applicable and most reliable in measuring the peptic action of malt extracts.

Another almost equally reliable criterion of the peptic strength is auto-digestion—the amount of coagulable albumen remaining in a malt extract after the same had been subject to the action of the peptonizing enzyme for a given period and at a given temperature being determined by means of heat coagulation.

At the beginning of this paper I have mentioned the application of these peptic malt extracts to practical brewing, and would like to add that by means of this principle the sensitiveness of the bottled product to low temperatures is minimized. Influences that have such detrimental effects on beer which has not attained stability to a high degree, are high temperatures, like pasteurization and summer temperatures, low temperatures, and light. All these effects are due to the presence, in unstable beer, of colloidal albumen, *i. e.*, albumen in a semi-soluble or unstable condition, and this albumen is influenced and gradually broken down by light or heat vibrations, and reverts to an insoluble state, as shown by chilling. By employing the digestive principle contained in malt, the colloidal albumen remaining in the beer after proper storage and natural treatment throughout, can be transformed before the beer reaches the bottle, into albumenoids that are desirable in every way, that is, into the permanently soluble and stable forms known as albumose and peptones.

At some future time I will make public the experimental data and details of these tests, which I have now been conducting for a number of years.

1135 FULLERTON AVE.
CHICAGO

DETERMINATION OF TOTAL FORMALDEHYDE IN FUMIGATORS AND COMMERCIAL SOLUTIONS¹

By JACK J. HINMAN, JR.

Many methods have been devised for the estimation of formaldehyde, most of which are designed for small amounts or mere traces, although the methods for the

¹ Presented at the meeting of the Chicago Section of the American Chemical Society, June 13, 1913.

¹ Read before the Indiana Section of the A. C. S., Indianapolis, June 13, 1913.

determination of formaldehyde in considerable amount are by no means few.

I have extended Craig's table of methods intending to give the principal ones which are said to be applicable to the analysis of strong solutions and solid polymers.

FORMALDEHYDE METHODS

Class I—Specific reactions:

- a. Ammonia to hexamethylenetetramine:
Legler, *Ber.*, **32**, 2841 (1899).
Trillat, *Compt. rend.*, **116**, 891 (1893); M. Klar, *Pharm. Zeit.*, **40**, 438 (1895).
Cirelli, *Arch. farm.*, **8**, 581-93.
Hermann, *Chem. Ztg.*, **35**, 25.
Schiff, *Chem. Ztg.*, **27**, 14 (1903); Gaillot, *Ann. chim. anal.*, **18**, 17-18 (1913); Malle, *Pharm. J.*, June, **1905**, p. 844.
- b. Potassium cyanide:
G. Romijn, *Z. anal. Chem.*, **36**, 18-27 (1897).
- c. Sodium hydroxide:
Legler, *Ber. d. deut. Ges.*, **16**, 133.
- d. Hydrazine sulfate:
E. Riegler, *Z. anal. Chem.*, **36**, iii, 115 (1887).
Rimini and Jona, *Giorn. Farm. Chem.*, **61**, 49-56.
- e. 4,4'-Dihydrazinodiphenyl hydrochloride:
Lebbin, *Pharm. Zeit.*, **42**, 18 (1897).
- f. Catechin:
Clauser, *Ber.*, **36**, 106 (1903).
- g. Sodium bisulfite:
C. Kleber, *Pharm. Rev.*, **22**, 1894 (1904).
M. Ripper, *Bull. soc. chim.*, [3] **31**, 691 (1904).
- h. Sodium sulfite:
Seyewetz and Gibello, *Chem. News*, **91**, 135, 2365.
Lemme, *Chem. Zeit.*, **27**, 896 (1903).

Class II—Addition products with elimination of water:

- a. Hydroxylamine:
Brochet and Cambier, *Compt. rend.*, **120**, 449 (1895).
- b. Aniline:
Trillat, *Compt. rend.*, **116**, 891 (1893).
M. Klar, *Pharm. Zeit.*, **40**, 548 (1895).
- c. Hydrazine hydrate:
Curtius and Pulvermacher, *Chem. Zeit.*, **26**, 701 (1902).
A. Pfaff, *Ber.*, **36**, 2360 (1903).
- d. Phloroglucin:
Clowes and Tollens, *Ber. d. chem. Ges.*, **32**, 2841.

Class III—Oxidation and reduction:

- a. Acid silver nitrate:
Grützner, *Arch. Pharm.*, **234**, 634 (1896).
- b. Alkaline silver nitrate:
L. Vanino, *Z. anal. Chem.*, **40**, 720 (1901).
- c. Acid potassium permanganate:
L. Vanino and E. Zeiter, *Z. anal. Chem.*, **40**, 587 (1901).
- d. Alkaline potassium permanganate:
H. M. Smith, *Analyst*, **21**, 148 (1896).
- e. Sodium hydroxide and hydrogen peroxide:
Blank and Finkenbeiner, *Ber.*, **31**, 2979 (1898).
Haywood and Smith, *J. Am. Chem. Soc.*, **27**, 1183 (1905).
Fresenius and Grünhut, *Z. anal. Chem.*, **44**, 13 (1905).
- f. Iodine:
Romijn, *Z. anal. Chem.*, **36**, 18 (1897).
Fresenius and Grünhut, *Z. anal. Chem.*, **44**, 13 (1905).
- g. Calcium oxychloride:
W. Brautigam, *Pharm. Zentr.*, **51**, 9156.
- h. Potassium bichromate:
Nieloux, *Bull. soc. chim.*, [3] **17**, 839.

Class IV—Physical methods:

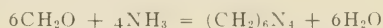
- a. Refractometer:
Richter and Jansen, *Chem. Weekblad.*, **9**, 1049.
- b. Specific gravity.

Investigations by A. G. Craig,¹ B. H. Smith,² Wallnitz,³ Romijn,⁴ and others have shown many of these to be untrustworthy. The general conclusions seem to be that of these methods the preferable ones are the potassium cyanide, iodine, ammonia, hydrogen

peroxide, and sulfite types. The potassium cyanide method is best adapted for dilute solutions and R. H. Williams¹ has shown the iodine method to be most readily influenced by normal impurities. For these reasons I chose methods from the three remaining types, since the solutions and polymers I wished to analyze were both strong and impure. Under the ammonia type I used Legler's and Schiff and Malle's procedures and repeated the latter, using ammonium sulfate instead of ammonium chloride. I also used the Blank and Finkenbeiner hydrogen peroxide method of the U. S. P., and Haywood and Smith's modification as given in *Bulletin 107* (revised) of the U. S. Bureau of Chemistry. The sulfite methods were those of Seyewetz and Gibello and C. Kleber. I also compared the refractometer tables of B. Wagner² and the calculation formula of Richter and Jansen based upon the refractometer reading. The references to these methods are given in the table above.

These methods were used in the analyses of four samples of commercial formaldehyde solutions, eight types of formaldehyde fumigators and a sample of Merck's trioxymethylene. In addition to normal impurities the fumigators contained various other substances such as naphthalene, phenol, glycerine and fats and all were more or less contaminated by rust. They were prepared for analysis, after removal from the tin cases, by separating the paraffin covering, and cutting into small pieces after scraping off as much iron rust as possible. The small pieces were mixed and preserved in rubber-stoppered bottles.

The ammonia method is based upon the reaction between ammonia and formaldehyde to form hexamethylene tetramine and water:



The gravimetric method has been found to be worthless as the tetramine loses weight indefinitely.

Legler's Method.—Weigh about 2 cc. of the solution (or 0.5 to 0.7 gram of polymers) into a glass-stoppered Erlenmeyer flask and add 50 cc. approximately normal ammonium hydroxide. Grease the stopper and let the tightly closed flask stand over night. Prepare two blanks using the same amount of the ammonium hydroxide solution and allow to stand the same length of time under the same conditions. Run in a slight excess of normal sulfuric acid and titrate back with normal sodium hydroxide, using rosolic acid as the indicator. The difference between the amount of normal acid used to neutralize the blank and the amount used in the case of the sample gives the amount of true normal ammonium hydroxide. Correct for the acidity of the sample.

1 cc. normal NH_4OH = 0.045 gram formaldehyde.

This method is known to give low results. Rosolic acid is not a satisfactory indicator. Loesekann recommends methyl orange titrated to full red.

Schiff and Malle's Method.—Introduce 20 cc. of neutral 20 per cent ammonium chloride solution into a glass-stoppered Erlenmeyer flask. Make a 1 to 10

¹ A. G. Craig, *J. Am. Chem. Soc.*, **23**, 638 (1901).

² B. H. Smith, *Ibid.*, **25**, 1028 (1903).

³ Wallnitz, *Deut. Gerber Ztg.*, **1**, **4**, **6**, **8**, **12**; through *J. Chem. Soc.*

⁴ Romijn, *Zeit. anal. Chem.*, [1] **36**, 18-24.

¹ R. H. Williams, *J. Am. Chem. Soc.*, **28**, 596 (1905).

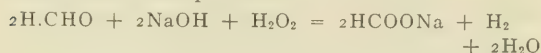
² B. Wagner, *Sonderhausen*, **1903**: booklet accompanying Zeiss' immersion refractometer.

dilution of formaldehyde and add 20 cc. to the ammonium chloride in the flask. Follow by 25 cc. of normal sodium hydroxide, grease the stopper and close tightly. Allow to stand one hour and titrate excess alkali with normal sulfuric acid, using rosolic acid as indicator. Correct for the acidity of the sample. When analyzing the solid formaldehyde use 0.5 to 0.7 gram and allow to stand over night.

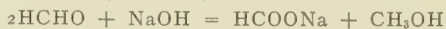
1 cc. normal NaOH consumed = 0.045 gram formaldehyde.

This method gave higher results than did the Legler method. Solution of the polymers in the liquid was not always complete after 12 hours' standing, however.

The hydrogen peroxide methods are based upon the oxidation of formaldehyde to formic acid and the neutralization of sodium hydroxide by it. The reaction which takes place is



According to Haywood and Smith another reaction may accompany this one, viz.:



This secondary reaction they claim leads occasionally to incorrect results and their method is intended to avoid this error. As a rule this method gave no lower results.

Blank and Finkenbeiner's Method (U. S. P.).—Three cc. of the solution or about 1 gram of the solidified formaldehyde is weighed into a glass-stoppered Erlenmeyer flask of about 500 cc. capacity: 50 cc. of normal sodium hydroxide solution and 50 cc. of hydrogen peroxide of known acidity are added, the latter run in slowly and through a funnel resting in the mouth of the flask. After foaming has ceased (about 10 minutes) rinse the funnel and walls of the flask with recently boiled distilled water and titrate the excess of alkali with normal sulfuric acid and litmus indicator. Correct for acidity of sample and the hydrogen peroxide used.

1 cc. normal NaOH consumed = 0.03002 gram formaldehyde (on O = 16 basis).

Haywood and Smith's Method (Bull. 107).—Put exactly 50 cc. normal sodium hydroxide into a 500 cc. Erlenmeyer flask and add 50 cc. of pure hydrogen peroxide of known acidity. Add 3 cc. of formaldehyde, whose specific gravity has been determined, through a pipette having an upper and lower graduation, holding the pipette so that it almost reaches the liquid in the flask. Put a funnel in the neck of the flask and heat on water bath for five minutes, shaking the flask occasionally. Cool to room temperature, wash funnel and sides of flask with recently boiled distilled water and titrate with normal sulfuric acid, using litmus indicator. Correct for the acidity of the sample and the hydrogen peroxide. When examining polymers use about 1 gram and heat on bath 5 minutes or until dissolved. This usually will not exceed the five minutes.

1 cc. normal NaOH consumed = 0.03002 gram formaldehyde.

The hydrogen peroxide methods have been recom-

mended as among the best for commercial solutions. The Blank and Finkenbeiner procedure usually gives results somewhat higher than the Haywood and Smith, however. The end point is fairly sharp.

The sulfite methods are based on the formation of the addition product, formaldehyde sodium bisulfite, when formaldehyde and sodium bisulfite are allowed to interact.

Seyewetz and Gibello's Method.—Prepare a 20 per cent solution of (dry basis) sodium sulfite and titrate 20 cc. to find the alkalinity. Dissolve 0.5 to 0.7 gram of the polymeric form in another 20 cc. of the solution in the cold and titrate with normal sulfuric acid to the disappearance of the red color. For the liquid form weigh about 2 cc. into a flask. Correct for the acidity of the sample and the alkalinity of the sodium sulfite solution. Use no more phenolphthalein than is necessary.

1 cc. normal acid = 0.03002 gram formaldehyde.

C. Kleber's Method.—Prepare a strong solution of commercial sodium bisulfite and add sodium hydroxide nearly CO_2 free, until the odor is destroyed. Dilute the solution so that 30 cc. equals 50 cc. normal sodium hydroxide, using phenolphthalein as indicator.

Use 5 cc. of formaldehyde solution, the specific gravity of which is known, and titrate with the bisulfite solution, using phenolphthalein until the red color just vanishes. Warm if necessary.

When examining polymers, warm about 2 grams in a little water and run in the bisulfite solution until the substance is entirely dissolved and the red color has disappeared.

1 cc. bisulfite solution = 0.05 gram formaldehyde.

These two sulfite methods are rapid, cheap and accurate. They approach the Haywood and Smith method quite closely. The Seyewetz and Gibello method resembles the Lemme method and the method of the 5th German Pharmacopoeia which have been highly recommended by Hampshire and Furnival,¹ Doby,² and Yamoto and Nakajima.³

The refractometric methods for formaldehyde solutions are not so accurate as the chemical methods on account of the interference of methyl alcohol and the polymers.

Richter and Jansen's Method.—The immersion refractometer should read 15.5 at 15° C. Make a one-to-one dilution of the formaldehyde solution with distilled water. Take the immersion refractometer reading of this solution at 15° C., subtract 15.5 from it, divide by 3.17 and multiply by two. This gives grams per 100 cc. Divide by the specific gravity to get per cent by weight.

B. Wagner's Table.—The immersion refractometer should read 15.0 at 17.5° C. Dilute as in preceding method. Take immersion reading at 17.5° C. Look up on table and obtain grams per 100 cc. Divide by specific gravity to obtain per cent by weight.

The dilution was necessary to get the reading within the scale of the instrument. The results were in good

¹ Hampshire and Furnival, *Pharm. J.*, **89**, 133 (1912).

² Doby, *Zeit. angew. Chem.*, **20**, 353-6 (March 1).

³ Yamoto and Nakajima, *J. Pharm. Soc. Japan*, **1910**, 871; through U. S. Hygienic Lab., *Bull.* **84**.

agreement among themselves. The result on the first sample was higher than the Blank and Finkenbeiner result, however.

No attempt was made to allow for errors introduced by the added substances, naphthalene, phenol, etc. The fats in sample L. 214 caused such variation in results that I did not complete the work with it.

The strength of solutions, the variation in measurement of volumes, the small amount of substance and the loss in weight during weighing tend to introduce inaccuracies. A difference of 0.1 cc. of normal solution means a difference of from 0.13 to 0.19 per cent in the result.

instead of titrations of excess material. For formaldehyde solutions they require the minimum of time, but when polymers are to be titrated the Kleber method is the most rapid of all. Sulfite methods are, of course, not applicable to the polymers gamma and delta polyoxymethylene and alpha trioxymethylene as described by Auerbach and Barschall.¹

For an occasional analysis, the methods of Haywood and Smith and Seyewetz and Gibello seem to be preferable, while in a plant producing formaldehyde or where a large number of samples are to be analyzed, Kleber's method would be the most desirable.

Legler's method gives too low results and Blank and

PERCENTAGE OF FORMALDEHYDE AS DETERMINED BY THE DIFFERENT METHODS

No.	Condition			Legler	Schiff		Blank	Haywood	Seyewetz		Richter
					and	Ammono-			and	and	
Old stock	Liquid	Slightly polymerized		36.11	Malle	sulfate	Finken'r	Smith	Gibello	C. Kleber	Wagner
X. 40	Liquid	Clear		36.30		36.05	37.20	37.09	35.67	36.44	37.42
X. 43	Liquid	Clear		35.46		36.79	36.42	36.73	36.27	36.17	36.74
X. 46	Liquid	Clear, greenish	Blk. sed.	36.88		37.16	37.67	37.02	36.84	37.45	37.60
Trioxymethylene	Powder			90.10		94.81	94.52	95.55	95.42	94.14	94.43
L. 208	Solid	Hard	Naphthalene	87.46		89.30	89.51	91.55	89.86	88.81	90.39
L. 209	Solid	Soft, waxy	Phenol and glycerine	61.94		64.00	64.06	64.90	64.63	63.96	63.84
L. 210	Solid	Soft, waxy		61.73		62.95	62.91	64.75	63.69	63.01	63.45
L. 211	Semi-solid	Mushy	Much rust	32.61	...	32.87	32.73
L. 212	Solid	Soft, waxy		62.78		62.93	63.16	64.43	63.45	63.08	62.97
L. 213	Solid	Hard		91.09		93.32	93.81	95.71	94.41	94.29	94.37
L. 214	Solid	Soft, greasy	Fats	46.32	40.53	45.12	45.71
L. 215	Solid	Soft, waxy		64.73		66.32	...	66.64	66.46	66.51	66.59

The end point with rosolic acid is difficult; the ammonia methods require standing for a considerable period of time and in the case of the Legler method the preparation of blanks is necessary.

The litmus end point is better than that of rosolic acid. The time required for the hydrogen peroxide methods is much less and the results are easily checked.

The end point in the sulfite processes is sharper than in either of the other types. The titrations are direct

Finkenbeiner's gave me the highest ones. Haywood and Smith's method gave slightly lower percentages than Blank and Finkenbeiner's, closely followed by Kleber's and the remaining methods.

My thanks are due to Mr. Rex Rudicel who assisted me in making the analyses.

CHEMICAL LABORATORY
CITY BOARD OF HEALTH
INDIANAPOLIS

LABORATORY AND PLANT

AN AUTOMATIC PIPETTE

By C. H. McCHARLES
Received July 7, 1913

A description of an automatic pipette was given in THIS JOURNAL by T. O. Smith (Vol. IV, p. 47). The apparatus described there has been used for a number of years in the laboratories of this station, but for a purpose quite different from that for which it was originally recommended. The lower end of tube C was placed above the zero mark on the burette and the tube C acted as a safeguard against overflow in case the three-way cock should be accidentally left partly open into A and B.

Smith's statement that "it is obvious that if the capillary tube is drawn out as fine as possible and the burette and container brought near the same level, the accuracy of the pipette is practically that of the burette" should be somewhat amplified. The automatic feature of this apparatus rests in the fact that liquid will rise in C to a point on a level with the surface of the liquid in A. This latter is not at all con-

stant in use, and its variation amounts to as much as six inches in smaller stock bottles and a foot in larger ones. If the tube C be drawn out so small that the volume of liquid contained in six inches to one foot of it shall be negligible in accurate pipette measurements, it would be so small that capillarity and cleanliness of its inner walls would influence the automatic level; and passage of air through it, especially when wet, would be altogether too slow for practical purposes.

The automatic pipette shown here in Fig. 1 differs from the above mentioned one only in that the point to which the liquid rises in C is constant. When liquid rises in D to the level H, the air supply to the syphon between A and B is closed and no more liquid enters D.

The dimensions given were found to be convenient, but the only required ones are:

1. E should be long enough to include the levels F and G as shown.

¹ Auerbach and Barschall, *Arb. Kais. Gesundheitsamti*, **27**, 183-230; *Chemical Abstracts*, **8**, 1125.

2. E should be of sufficient volume below G to prevent air from entering the syphon between A and E while filling the burette.

3. The side opening I prevents air bubbles from entering the syphon.

4. D should be of sufficient volume below H to prevent breaking the syphon between D and B. A four or six ounce salt-mouth bottle serves the purpose.

5. C must extend above H.

deterioration. This could be obtained from any glass-blower.

NUTRITION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

IMPROVED GOOCH CRUCIBLE HOLDER

By LORIN H. BAILEY
Received June 30, 1913

There have been developed in the Bureau of Chemistry several forms of Gooch crucible holders. Each form, while differing somewhat in detail from the others, has for its foundation principle the substitution of a solid rubber holder for the rubber-covered glass Gooch holder which has been in almost universal use. The particular form shown in the accompanying illustration has been in use in the Plant Chemistry Laboratory for about a year and has given good satisfaction. It has also met the approval of a number of visiting chemists.

This holder is made to fit an ordinary 2-inch funnel which is inserted in a regular suction flask. The upper edge of the holder projects over the edge of the funnel and thus makes the seal. The lower edge of the holder rests on the side of the funnel and supports the holder when the suction is on the flask. The opening is made to conform to the size of the 25 cc. porcelain Gooch crucible, and the lower surface of the crucible projects beyond the holder so that the filtrate does not come in contact with it. These holders can be cut from No. 12 rubber stoppers, which was at first done, or they can be obtained already molded from some of the large chemical-apparatus supply houses.

BUREAU OF CHEMISTRY
WASHINGTON

NOTE ON PRODUCER GAS ANALYSIS

By JAMES C. VAIL
Received June 26, 1913

In the analysis of producer gas with the Williams modification of the Orsat apparatus or with Morehead apparatus the residual gas after the absorption of CO_2 , illuminants, O and CO in the usual manner is often too lean to be exploded without the addition of hydrogen. As there may be a certain amount of inconvenience and some uncertainty as to the purity of the hydrogen, I have found the following procedure more satisfactory for enriching the gas to a point where it may readily be made to explode. After the usual absorptions CO_2 , illuminants, O, CO, the residual gas is passed into the CO_2 absorption pipette or into the reservoir provided for the purpose in the Morehead apparatus and the measuring burette filled with water (acidified with sulfuric acid) which has previously been cooled to room temperature. A current of 6 or 8 volts passed between the electrodes used for the explosion will quickly produce enough of

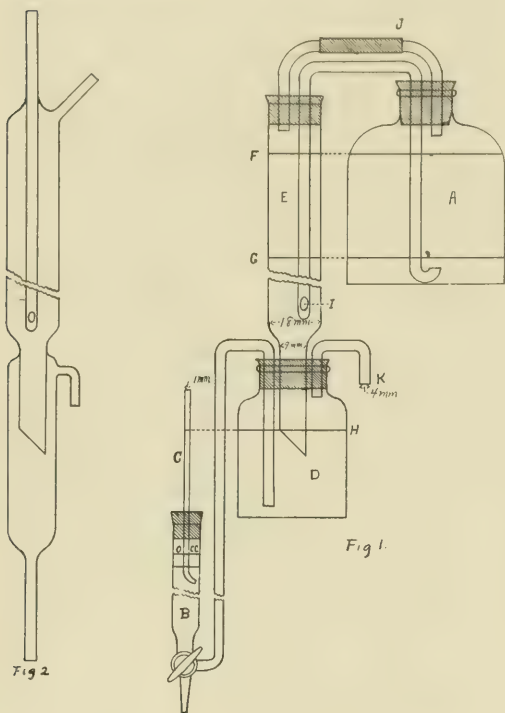
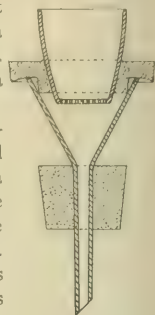


Fig. 1 represents an arrangement for use of liquids which must not be permitted to come in contact with rubber. A silver stopcock permits the use of lye. When this precaution is not necessary the container A may be stoppered with a one-hole stopper bearing a glass tube corresponding to the lower end of E, which in turn is inserted in D inverted. A and D are now inverted and placed on a support and B connected as in Fig. 1. This eliminates E and its connections.

In order to fill the syphon shown in Fig. 1, the air passage is disconnected at J and pinched. Apply suction to a rubber tube connected to K, and bearing a pinch-cock, till D is filled. Close the pinch-cock, connect J, fill B by suction applied to C, and remove the rubber tube from K.

By regulating the height of the lower end of C, the burette may be adjusted to deliver any desired volume.

Fig. 2 represents a form of apparatus which would eliminate two rubber stoppers and all inconvenience arising from the leaks which they develop upon



a mixture of hydrogen and oxygen in molecular proportions to sufficiently enrich the gas. This volume is read off and a sample added and the whole diluted with air and, after thorough mixture, exploded in the usual manner.

This simplifies the calculation of results as the volume

of hydrogen-oxygen mixture added may be subtracted from the total contraction due to explosion and the H and CH_4 and N calculated as though it had not been necessary to enrich the gas.

CHESTER, PA.

ADDRESSES

THE CHEMICAL INDUSTRIES AND THE UNIVERSITIES¹

By MARSTON TAYLOR BOGERT

Before this audience it is wholly unnecessary to dwell upon the tremendous importance of chemistry to the material growth and prosperity of the nation, or its vital bearing upon the health and happiness of the individual. Suffice it to point out that the amount of a country's appreciation of the value of chemistry in its development and the extent to which it fosters the manifold applications of this science in its every-day life is generally a measure not only of the industrial progress and supremacy of that country, but also of its real civilization.

Two of the most important factors in the advancement of chemistry are the universities and the chemical industries, and it is consequently a matter of concern to all of us whether they are working together at present to the best advantage or not. My own observation leads me to believe that they are not, and this address is intended primarily to indicate some of the lines along which it seems to me there might be much closer coöperation.

As the majority of my fellow-members are themselves manufacturers, or are connected in one way or another with our chemical industries, I shall endeavor to present the case principally from the university side, and I trust that what I shall have to say will be judged from this point of view.

Robinson has defined education as "the process of fitting the individual to take his place and do his part in the life of his age and nation," and no educational institution at the present day can discharge its responsibilities faithfully unless it accords, in its equipment and in its curricula, adequate recognition to so comprehensive a science as chemistry, which in its wide sweep, in one way or another, touches almost every phase of human life and endeavor. That our universities are realizing this more clearly every day seems evidenced by the frequent construction of new laboratories and the steadily increasing size of the chemical staff. It is worth noting that, almost without exception, additional laboratory accommodations are immediately taken up by an increased number of students. As indicative of the extent to which chemistry enters into our modern university curricula, I may be permitted to refer to my own Alma Mater, Columbia University, where this subject is taught under seven of the eleven constituent faculties; and, as proof of the demand for higher education in this same field, I would call attention to the doctorates conferred in 1911 (the latest compilation I have seen; *Science*, N. S., 36, 129, Aug. 2/12) by the leading universities of the United States, when more than twice as many were awarded in chemistry as in any other subject (78 out of a total of 492), the nearest competitor being English (with 34).

The universities are active in everything which concerns the life and welfare of the nation, and it can be truly said of them, in the words of Terence, "humani nil a me alienum puto." So far as the chemical industries are concerned, it should not be overlooked that the universities, in addition to training chemists, also educate men for the non-chemical positions, whether clerical, financial, or commercial; and that everything which they accom-

plish to increase the security of the rights of the individual or of property, or which ministers to the general prosperity, comfort and happiness of the nation, is obviously of direct advantage to the chemical manufacturer as well, and in all such matters therefore the universities have the right to expect cordial and active coöperation on the part of our chemical industries.

In the training of men for the chemical profession we are all immediately interested, and in this direction the universities are doing the best they can with staff and equipment available and with the raw material represented by the student body. Equipment and staff are increased as funds are provided and entrance and graduation requirements steadily advance.

The chemical industries can and do coöperate by giving employment to properly trained and qualified graduates; and higher training, as represented for example by a higher degree should, other things being at all approximately equal, secure for a man a higher initial salary. It goes without saying that the salary should in any event be a fair one, commensurate with the service the man is expected to render, and with good chance of promotion for demonstrated efficiency and ability. In many cases, chemists employed by manufacturing concerns are required to execute iron-clad contracts by which they definitely waive all patent rights to anything they may discover while in the employ of the company. These discoveries then become the property of the employer, who is under no legal obligation to remunerate his chemist therefor. Employers, however, who are really desirous of assisting the universities in their work of training chemists, will see to it that their chemists are well rewarded for all discoveries of value.

Many of our leading chemical manufacturers have coöperated with the universities very helpfully with advice and suggestions in arranging the most effective curriculum for the training of the industrial or engineering chemist. But the curriculum is not everything, and even with the best one possible it is not an easy matter to turn out men who, in addition to adequate scientific training, are clear-headed and masterful, honorable and dependable, sober and of high moral tone, of broad and creative scholarship and conspicuous inventive ability, of unwearied energy, and with the necessary health and physique to stand plenty of hard work. Of course, such paragons are scarce and much sought for in all lines of human activity. Nor is it ordinarily feasible for a university to turn out men who are experts in the manufacturing details of the various lines of chemical industry. The best they can do is to give their men the necessary broad, theoretical and practical foundation upon which all lines of chemical manufacturing rest. Munitiae can be learned only in special schools or, preferably, in the plant itself, and manufacturers can help here by giving a good man a chance to learn these details. Many a high-class university graduate has lost his first position because of his employer's impatience in this respect. And yet, if the manufacturer but knew it, he is often throwing away gold and accepting dross in exchange. The properly trained chemical graduate is, in the vast majority of cases, a far more valuable man to a chemical concern than the employee who knows only mechanical details and has not had the benefit of any real scientific education. At first the latter may appear to greater advantage because of his familiarity with

¹ President's address at the thirty-second annual general meeting of the Society of Chemical Industry, Liverpool, England, July 16, 1913. Reproduced from the *Journal of the Society of Chemical Industry*, 14, 720.

the processes involved, but he will be very speedily outstripped by the university man given at all a similar initial endowment. One is likely to be a mere rule-of-thumb man, whose actions are determined wholly by previous experience and who is completely lost when anything new and totally unexpected occurs. The other is the more resourceful, and will seek the underlying cause of the difficulty and independently endeavor to work out a remedy. Each has his place in our industrial life, but the scientifically trained man has surely the brighter and more promising future before him, and will rise to higher levels of usefulness.

On the other hand, university teachers often appear inefficiently posted on the type of men needed in chemical industry, and ignorant of the fact that a man admirably suited for the research laboratory is not necessarily equally well fitted for the career of an engineering chemist or works manager. To my mind, no greater unkindness can be done to a student than to secure for him a position for which he is not properly qualified, only to see him struggle along through the best years of his life and awaken finally, perhaps too late to begin another career, to a keenly painful realization of the fact that he is but a square peg in a round hole. It is a heavy burden of responsibility, and one not to be shirked or avoided, this advising of students about to embark upon the uncertain sea of life's work for which port to steer, but it is also a splendid opportunity for high personal and public service and should be so esteemed. Few talents are more valuable to the teacher than the ability to gauge accurately a student's character and capabilities, and this genius is likewise potent in the business world, for I have heard more than one great captain of industry say that he owed his success to his knowledge of men more than to any other one thing. Employers are entitled to a perfectly frank and accurate statement concerning an applicant's qualifications—a statement which sets forth the candidate's weak points as well as his strong ones, and it does not take them very long to find out from whom they may expect such statements.

But I would not have you overlook, nor do I intend to dismiss quite so briefly, the importance of manual training, for it is a subject very much to the fore with us in the United States just now and of vital concern to all manufacturers. Every factory, in addition to capable management, up-to-date mechanical equipment and suitable research laboratories, must have in its employees technical skill equal to that of its competitors, domestic and foreign, or it cannot hope to win in the struggle. To obtain in our workmen this high degree of manual dexterity and industrial efficiency, there is need for active coöperation between our educational institutions, our factories and our labor unions. It is far better to market the results of high-grade labor than merely to realize on raw material. To illustrate the point, let me quote from a recent report of a special committee of the National Manufacturers' Association of the United States, citing conditions now obtaining there:

"We sell our cotton to Switzerland at 14 cents a pound, with scarce any labor in it. We buy it back in the form of fine handkerchiefs at \$40 a pound, all labor. We export bar iron and import razor blades; export hides and import gloves; export copper and import art bronzes." In the year 1911, 56 per cent of the total exports of manufactured articles from the United States carried only from 3 to 15 per cent of factory labor.

Perhaps the greatest opportunity of all for coöperation between the universities and the chemical industries, and the one where in many countries such coöperation is conspicuously lacking, is in extending the boundaries of human knowledge by original investigation and research. Here, too, the universities and technical schools are doing what they can, with insufficient funds and equipment, and with an overburdened staff, to serve the community and the chemical industries, both by conducting original research themselves, and by throwing open their great libraries and occasionally certain of their laboratories for the

solution of problems of financial value to the manufacturer. The latter, in return, can assist by supplying raw material, additional funds, and knowledge gained in the laboratories of the plant.

When a chemical industry has problems to be solved, these problems can be attacked either inside or outside of the plant. If the policy of the management is that all chemical problems are to be studied only within the establishment, a research laboratory or at least a research chemist must be provided for the plant or for the company. At present, in the United States, probably not more than 75 or 100 manufacturing establishments have research laboratories or employ research chemists. In Germany, and perhaps also here in England, such research laboratories in association with chemical industries are much more common. The great laboratories of the Badische Anilin und Soda Fabrik and of the Elberfeld Company are good examples of the importance attached to such research work in Germany, and it would be difficult to adduce any stronger argument in support of its value than the marvellous achievements of these huge concerns.

A frequent difficulty encountered in the employment of research chemists or the establishment of a research laboratory is that many a manufacturer does not appear to grasp the need or importance of such work, nor know how to treat the men in charge so as to secure the best results. The owner may not even fully understand just what is the cause of his manufacturing losses or to whom to turn for aid. If he finally engages a chemist he is apt to look upon him as a sort of necromancer who should be able to accomplish wonders, and if he cannot see results in the course of a few months is likely to consider the investment a bad one and regard chemists as a class as a poor and useless lot. It is not unusual for the chemist to be told to stick to his laboratory and not go prowling about the works, and he must also face the natural opposition of workmen to any innovations and reckon with the jealousies of foremen and of various superior officials so that, like the policemen in the "Pirates of Penzance," often his "lot is not a happy one."

From the standpoint of the manufacturer, one weighty advantage of the policy of having all problems worked out within the plant is that the results secured are not divulged, but are stored away in the laboratory archives and become part of the assets and working capital of the corporation which has paid for them; and it is usually not until patent applications are filed that this knowledge, generally only partially and imperfectly, is made known to the public. When it is not deemed necessary to take out patents, such knowledge remains buried.

In this matter of the dissemination of knowledge concerning industrial chemical practice, it must be evident to all that there is but little coöperation between the manufacturers and the universities. The crux of the difficulty lies just here. Chemical manufacturers, as just stated, are quite naturally averse to publishing any discoveries made in their plants, since "knowledge is power" in manufacturing as elsewhere, and new knowledge gained in the laboratories of the corporation may often very properly be regarded as among the most valuable assets of the concern. The universities, on the other hand, exist for the spreading of knowledge, and from their standpoint the great disadvantage of the above policy is this locking up of knowledge, for it effects a serious retardation of the general growth and development of the science in its broader aspects, and renders it much more difficult for the universities to train men properly for such industries, since all textbooks and general knowledge available would, in all probability, be far behind the actual manufacturing practice. I believe that all familiar with the situation will admit that this is a real problem and one constituting a serious handicap to those endeavoring to give up-to-date instruction in industrial chemistry. One immediately harmful effect that the above policy has upon the universities

is that it not infrequently results in some of their most capable investigators spending many of the best years of their lives and considerable sums of money in attempts to solve problems, the clues or answers to which had been discovered and filed away long before in the laboratory records of the factories.

Of course, the universities must also contend with the fact that the larger manufacturing establishments can usually offer much better salaries to skilful chemical investigators, and thus withdraw from university work some of the best men.

All who have had any experience in such matters know how difficult it is to secure papers for the programs of our Sections, or for our Journal, from men engaged in industrial chemistry, the usual reply the manufacturer gives to such solicitations being to the effect that he is in business to make money and is not running an educational institution.

It is not to be expected that the manufacturers will promptly publish to the world, upon demand, their most cherished "trade secrets," and it would of course be useless to make any such request. But in almost all great chemical industrial establishments which have been in operation for any length of time, information has been accumulated in the course of the work which could be made known without injury to the firm concerned, and to the considerable advantage of the chemical world-at-large. For example, it not infrequently happens that a corporation permanently abandons one line of work, either because local conditions have made it no longer profitable or because it wishes to devote itself to other more lucrative ones. In such cases there seems no good reason why the knowledge gained in connection with the abandoned process or product should not be made public. Or, it may be, the analytical laboratory finds some convenient rapid method to take the place of a more laborious one, or devises new apparatus for old laboratory processes. Other cases might be cited were there time.

A very welcome form of coöperation, therefore, would be that of keeping the university teachers better posted on present-day manufacturing practice, so that they could point out more clearly the applications to industry of the principles they were endeavoring to inculcate, and call attention to the rapid approximate commercial analytical processes and short cuts used in the factories in addition to the longer and more accurate methods generally taught in analytical laboratories. Were the teacher more familiar with industrial wastes and by-products, he could often select problems for his advanced research students with reference thereto and thus considerably heighten their interest in the work.

It is well said in the Reports of the Twelfth Census of the United States that "Probably no science has done so much as chemistry in revealing the hidden possibilities of the wastes and by-products in manufactures. This science has been the most fruitful agent in the conversion of the refuse of manufacturing operations into products of industrial value. . . . Chemistry is the intelligence department of industry." Yet the teacher is often uninformed concerning the character and amount of the by-products going to waste in his immediate neighborhood, a careful study of which might lead not only to financial reward for the manufacturer as well as for himself, but might also save us much of the present pollution of our streams and of the air we breathe.

It is not only now very desirable, but will soon become imperative for our manufacturers to avail themselves more freely of the assistance of the experts in our universities and technical schools. That nation will unquestionably make the longest strides in commercial development which sells goods carrying the maximum of brains and the minimum of raw material. Germany has already learned this, and is rapidly forging ahead as the natural result. England and America must follow that lead or ultimately find themselves far in the rear. Any country, like my own, thanks to a wonderful endowment of natural re-

sources, and to protective tariff walls, may, for a time, appear to be holding its own in the world's trade without adopting the above policy; but it is only because of these peculiar local conditions that we have been spared the embarrassment of close international comparisons. Our tariff walls are already tottering, and the lavish use of natural resources is but a spendthrift squandering of a priceless and irreplaceable heritage, and the end of that, too, is in sight with a continuance of present methods. The day is already at hand, for America at least, when manufacturers must scrutinize more closely the efficiency of their plants with reference to raw material consumed, for human intelligence is the one resource which increases with use, forever and immeasurably, and the cultivation of which furnishes the only substantial basis of prosperity, progress and happiness.

In the United States we have been wont to boast of our huge agricultural exports, but, as President Wallace said at a recent Conservation Congress, "the nineteenth century farmer was no farmer at all; he was a miner, mining the fertility of the soil, and selling it for the bare cost of the mining;" since every bushel of wheat exported carries with it approximately 27 cents worth of phosphorus, every bushel of corn 13 cents, every pound of cotton 3 cents, figures which equal the supposed profits of the transaction. How we are to replenish our stock of phosphorus, if once exhausted, is not yet clear, although, so far as we now know, the race itself must perish without an adequate supply of this element.

There are but four great manufacturing nations in the world—England, Germany, France, and the United States. Outside these four, and looking to them for their manufactured articles, stand the one and a half billion human beings in the rest of the world. The prizes to be won in this international trade are beyond compare. They are to be measured not only in money, but also in intellectual advancement, in closer bonds of international friendship, mutual respect and esteem, in national spirit, and in heightened civilization.

Any manufacturer who feels unable to coöperate as suggested above, should at least be willing to support generously those agencies upon whom now falls the chief burden of disseminating knowledge—notably our educational institutions and our chemical journals, such as the Journal of this Society.

Or, if he still demurs, there are other lines open. Few manufacturing concerns feel inclined or called upon to establish extensive libraries within their plants, and it would appear, therefore, to be to their own immediate interest to provide whatever funds might be needed to supply the library of the nearest university or technical school with all books likely to be of service to the various experts of the plant. This also would bring them into closer personal touch and sympathy with the officers of instruction there.

Any manufacturer having an important chemical problem to solve in connection with his business, and without the proper staff or equipment to attack it within the plant, must look outside for assistance, and he then has the choice of the private commercial or research laboratory on the one hand, or the universities and technical schools on the other.

The advantages and disadvantages of the private research laboratory, at least in so far as they relate to the availability of the new knowledge thus discovered, are much the same as those already pointed out for the factory research laboratory.

If the manufacturer elects to refer his problem to the university or technical school, such reference is most likely to take the form of an industrial fellowship and there is much to be said in favor of these fellowships. They allow the donor to keep secret for two or three years the results secured, after which they can be published. They also secure to him patent rights. They give highly specialized training to good men and often secure for them permanent employment and a share in the profits of their discoveries. It should be obvious at the outset that a

fellowship of this character can be successful only when there are close confidential relations subsisting between the manufacturer and the officer in charge of the research. No cooperation can be really effective unless based upon a thorough mutual familiarity with conditions and an abiding faith in the integrity and sincerity of purpose of each other. It is likely to prove a poor investment for a manufacturer to seek the aid of an investigator if he is unwilling to take such expert into his confidence. I have occasionally had manufacturers apply to me for the solution of a problem affecting their industry and, when I asked how they were actually carrying out the process in the factory, have had them say politely that they preferred not to answer any questions concerning the operations of their factory and that all I was asked to do was to see what I could accomplish in my own laboratory. Of course the answer to such a proposition should be a decided negative, since its acceptance would almost invariably result to the mutual dissatisfaction of both parties concerned.

It would seem manifest that no one man is competent to direct original research in all lines of industrial chemistry, and that the wisest course for a manufacturer to pursue when contemplating the establishment of a research fellowship would be to secure the aid of the particular university officer whose experience and personal achievements entitle him to be considered an expert in that special field, and who has the necessary equipment and location to attack such a problem with good chances of success, and then to arrange to provide him with such funds as may be required for assistants or for raw material.

In the case of divergent reports from chemical experts, the university laboratory is the natural court of appeal for an impartial verdict.

The most urgent need of the day is, in my judgment, the endowment of chemical research, either by the establishment of research professorships or, still better, by founding great chemical research institutes in affiliation with our chief universities for the study of problems both in pure and in applied chemistry. The splendid Kaiser Wilhelm Institute for Chemistry, recently opened in Berlin, thanks to the active and generous assistance of His Majesty the German Emperor, is the first of its kind in the world, and its advent should be hailed with delight as indicating the dawn of a new and brilliant era for our science. It is worth noting that the policy of this research institute is the man first, the equipment afterwards, and the group of distinguished investigators now gathered together there witnesses to the wisdom of this plan. If we would not be outstripped by our friends across the water, we must have similar establishments here in England and that, too, speedily. The benefits which will accrue to the nation from the labors of such research institutes manned by our keenest investigators are truly inestimable, and it is to be hoped that this remarkable opportunity will appeal to the imagination and the generosity of other far-sighted benefactors of mankind. Much has been done, and worthily done, in all of our great cities for the cause of medicine, for example, whereas chemistry, except in Germany, still appeals in vain for similar recognition. Yet the dependence of medicine, and of life itself, upon chemistry is seen more clearly every day, and he who now still has doubts upon the subject has but to read the recent remarkable presidential address of Dr. Schäfer before the Dundee meeting of the British Association for the Advancement of Science (1912), in which, after calling attention to the few elements and simple inorganic compounds making up living substance, he says: "The combination of these elements into a colloidal compound represent the chemical basis of life; and when the chemist succeeds in building up this compound, it will, without doubt, be found to exhibit the phenomena which we are in the habit of associating with the term 'life.'" He further suggests the possibility "that heredity also is one of the questions, the eventual solution of which we must look to the chemist

to provide," and, as already indicated, the maintenance of any human life whatever upon this planet of ours depends absolutely upon the labors of the chemist.

In the sphere of industrial chemistry such a research institute might well take the form of laboratories "especially equipped with the standard appliances for executing industrial operations, and provided with all the means for the prompt, proper and accurate determination of experimental data, in a way and on a scale which would make this data available for factory application," as has been suggested already by Professor Whitaker, the Chairman of our New York Section (*THIS JOURNAL*, 3, 797), and since, as he points out, few if any laboratories now exist where researches can be undertaken "which involve single and multiple effect distillation, evaporation, filtration, calcination, condensation, absorption, drying, controlled temperature reactions, vacuum and special atmosphere reactions," and the like.

The really important thing is to bring together the problem and the man competent to solve it. Skilful investigators are often wholly unaware of many of the important industrial problems calling for solution, and the great manufacturing concerns are often equally ignorant concerning the men in the country best qualified to solve these problems. If it were possible to establish some sort of a clearing-house committee, composed of representatives of the universities and of the manufacturers to bring investigator and problem together, it could render immense service to the country. If the research institutes proposed above were established, their Boards of Direction might perhaps perform such a function. In fact, the matter is so important that there would seem ample justification for the general Government itself to take cognizance of it, since it concerns the prosperity of the whole nation, and refer it to an appropriate committee or board, in conjunction with its other activities for the benefit of our manufacturing industries.

Some of our wisest and most far-sighted manufacturers feel that there is urgent need for what might be termed an Industrial Efficiency Corporation, with a staff of experts in all lines of chemical manufacturing, to whom any manufacturer might refer for solution all problems affecting his plant. If the details of such an organization can be satisfactorily worked out, this corporation can render much of the service indicated above, but it too will have to overcome the reluctance of many manufacturers to allow any other man, or group of men, to know what they are actually doing in their factories.

There is room also for better cooperation in the matter of patents. The university teacher is usually at a heavy disadvantage in endeavoring to obtain a fair trial of his inventions and a reasonable share in the profits. In this connection the establishment here of the Letters Patent Insurance Co., Ltd., and in the United States of the Research Corporation, are of interest.

The latter is described as "an experiment in the public administration of patent rights" (F. G. Cottrell, *THIS JOURNAL*, 4, 864). It was incorporated February 26, 1912, as a stock company, under the laws of the State of New York, with offices at 63 Wall Street, New York City, its declared purposes being:

(a) To receive by gift and to acquire by purchase or otherwise, inventions, patent rights and letters patent either of the United States or of foreign countries, and to hold, manage, use, develop, manufacture, instal, and operate the same, and to conduct commercial operations under or in connection with the development of such inventions, patent rights and letters patent, and to sell, license, or otherwise dispose of the same, and to collect royalties thereon, and to experiment with and test the validity and value thereof, and to render the same more available and effective in the useful arts and manufactures and for scientific purposes and otherwise.

(b) To provide means for the advancement and extension of

technical and scientific investigation, research and experimentation, by contributing the net earnings of the Corporation, over and above such sum or sums as may be reserved or retained and held as an endowment fund or working capital, and also such other moneys and property belonging to the Corporation as the Board of Directors shall, from time to time, deem proper, to the Smithsonian Institution, and such other scientific and educational institutions and societies as the Board of Directors may, from time to time, select in order to enable such institutions and societies to conduct such investigation, research and experimentation.

(c) To receive, hold and manage, and dispose of such other moneys and property, including the stock of this and of any other corporation, as may, from time to time, be given to or acquired by this Corporation in the furtherance of its corporate purposes, and to apply the same, and the proceeds or income thereof, to the objects specified in the preceding paragraph."

To summarize briefly, the purposes of the Corporation are to control patents for the benefit of the public, and to aid research.

It is expected that the duties of the Corporation will be largely administrative, the actual practical work in connection with the patents being conducted either in coöperation with the manufacturing plants or with the universities and technical schools. These administrative expenses for the first year are estimated at \$10,000, and have been provided for by subscriptions to the stock of the Corporation, which stock it is expressly stipulated shall pay no dividends whatever, but may be repurchased at any time at par by the Board of Directors, and no stock can be disposed of without first giving the Board an opportunity to exercise this option. After the first year, it is expected that the undertaking will be self-supporting.

It appears to be the intention of the Corporation for the first few years to consider only such patents as may be offered as outright gifts, and Dr. Cottrell, in the article cited, says, "present indications are that the latter (the Corporation) will find itself well occupied even by these offers alone." In other cases, patentees may be willing, it is hoped, to assign to the Corporation their patent rights within certain geographical boundaries, retaining the rest for themselves; or perhaps present to the Corporation the rights to use the patents in connection with certain lines of manufacturing and retain for themselves the rights for other lines.

The real actuating cause in the establishment of this Corporation has been the fine self-sacrificing generosity of Dr. Cottrell himself in turning over his own valuable patents on the electrostatic collection of smoke and fumes, thus voluntarily relinquishing what promises to be large profits. Too much cannot be said in praise of such a splendid example of altruism, and it is to be hoped that many others may be found to follow this example of real patriotism. It has been urged that had such an organization been in existence at the time the Diamond Match Company generously threw open to all its sesquifuldite patents, it might have been willing to turn them over to this Research Corporation for the benefit of chemical investigation.

The experiment is an exceedingly interesting one and surely we all wish it the greatest measure of success.

True, in the United States (Patent Act of March 3rd, 1883) and perhaps also here in England, patents may be formally issued as free to the public without royalty of any kind, and for these patents the Government collects no fees. One reason why such regulations have not accomplished as much as their advocates hoped for is that they fail to provide adequate protection to the manufacturer who invests the large sums necessary in plant, equipment and advertising, to market successfully a new article.

There is also need for cooperation in some countries in securing an efficient and equitable system of patent laws, and in obtaining fair and impartial legislation where our chemical industries are

concerned; cooperation which, on the one hand, shall protect our manufacturers from unjust laws or regulations and which, on the other hand, shall effectually safeguard the community against any inroads upon their rights by the manufacturers.

For example, a Government might propose legislation classing as adulterated any foodstuff containing 10 per cent of arsenic. If the university experts knew that such a percentage of arsenic was normally present in certain perfectly wholesome and unadulterated natural foods, it would be their duty to call the attention of the law-making body to the fact, that the proposed legislation might be amended accordingly.

To take the other side: if it appeared that any line of industry, by combinations at home and the erection of a tariff wall against imported articles, was effectually stifling all competition in order that it might continue old-fashioned, wasteful and inefficient methods of manufacture, and charge the public high prices for their goods, that public is entitled to redress and will surely obtain it sooner or later, and it would be the duty of the university officers to make clear to the community the extent to which they were being imposed upon by the offending manufacturers.

In the building up at our larger universities of museums illustrating the development and present status of industrial chemistry, there is afforded a field for coöperation not yet very extensively made use of. The exhibits themselves must, in the nature of the case, be contributed chiefly by the manufacturers, and should include full sets of samples of all products—initial, intermediate and final—as well as working models of the mechanical parts of the process, so that the student may see represented before him all the various steps in the manufacture: the university, on its part, to provide suitable housing and display cases, to look after the proper assorting, arrangement, distribution and labelling of the material, and the necessary care and upkeep of the same. What such collections mean to the teacher of chemistry, no one appreciates better than the Columbia University man, for there we have had for more than a generation the extensive Chandler Museum of Chemistry, contributed largely by our chemical manufacturers, and gathered together patiently and with tireless energy and enthusiasm by that Nestor of American chemists, the first American President of this Society, our own dear Dr. Chandler.

Such museums are not only for the benefit of the university but are for public exhibition as well, and in addition to these university museums, or replacing them, are the great industrial museums of the world like the Deutsches Museum of Munich and the South Kensington of London, and it is a genuine inspiration to see these places thronged with young and old watching closely the operation of the working models exhibited, examining critically the various products, or listening to the explanatory remarks of an accompanying teacher or of an attendant. But we need to add to the equipment of those museums we now have and to assist in the creation of others, for they illustrate most graphically the commercial and industrial resources of the country and provide a telling object lesson of the significance of chemistry in the utilization and development of those resources.

When the layman sees before him a barrel of coal tar, it is to him only a black, evil-smelling viscous mass; but when he sees growing out of that barrel, a tree-like arrangement of the innumerable substances obtainable therefrom—first the primary products, then the secondary, and so on, until at the ends of the branches he surveys all the wonderful dyestuffs, drugs and perfumes manufactured from this same foul mass—it takes on for him a wholly new aspect and interest.

A block of wood is a very commonplace article, but when that block of wood stands side by side with some of the beautiful and useful products which chemistry can conjure therefrom, the observer begins to have some inkling of the magic of science and its potent influence in the progress of civilization.

Lest I weary you, I will but touch upon one other opportunity for cooperation, and that is in the organization of chemists' clubs, where the members of the profession may regularly foregather and the university man rub shoulders with his manufacturing brother. A chemists' club is a most excellent reagent for blending together in one homogeneous, harmonious whole all brands of chemists, and it is quite true that a happy union of theoretical and practical chemists can often be accomplished most pleasantly by clubbing them into it. Our Chemists' Club in New York has brought together, in one big contented family, all the chemists of that metropolitan district, and its influence has extended over the length and breadth of the United States. After all, friendship is the main thing between brother chemists, and I had rather have a colleague's intimate and warm-hearted friendship for me personally than merely his respect and admiration for my scientific achievements.

To recapitulate briefly, the university exists for the community, and its supreme desire is to render ever better and more efficient service. It is the servant of our chemical industries and their agent in the training of the men needed by these industries. It seeks closer cooperation from them in disseminating knowledge and in extending its boundaries, in endowing chemical research and chemical publications, in aiding our chemical libraries, in the matter of patents and legislation, in the creation of great museums of peaceful arts, in the organization of chemists' clubs and the provision of suitable buildings therefor, and in countless other ways, and if this short and very imperfect presentation of the subject serves in any way to arouse increased interest in these matters, it will have been worth while. Efficiency is the only sure path to supremacy in any field of human endeavor, and closer cooperation between our universities and our industries will go far to assure increased efficiency to both.

COLUMBIA UNIVERSITY
NEW YORK CITY

DEPRECIATION AND OBSOLESCENCE¹

By RICHARD K. MEADE

The capital invested in any manufacturing enterprise may be appropriately distributed among the following items:

- (1) Plant.
- (2) Working capital.
- (3) Good will and patent rights.
- (4) Laboratory and office buildings and their equipment.
- (5) Mill site, real estate, mines, quarries, etc.
- (6) The cost of financing.

Of these various items, a few may be expected to increase in value as time goes on without any special provision other than that ordinarily attended with successful operation of the business. Other items become less even under the most careful management. "Good will" of course increases in value under successful management. The working capital may or may not be increased according to the policy of those at the head of the organization. The real estate will increase or decrease in value according to local conditions. The value of patent-rights grows less as the time of the monopoly granted under them diminishes. On the other hand, where processes are employed under a royalty, the expiration of the life of the patent will allow these to be used without such expense. The deposits of raw material, of course, decrease in value as they are drawn on to supply the plant. That portion of the capital which was devoted to raising the rest represents nothing of actual tangible value, although it is something with which practically all manufacturing enterprises have to reckon.

The value of the plant unquestionably gets less as time passes and the only way in which it can be maintained at anything like its original value, is by continually repairing the machinery and apparatus and by replacing worn-out parts by new ones. Even

when this is done, however, there comes a time when such replacement of parts will not be sufficient to keep the plant operating economically either because the cost of the repairs themselves is too great or else because the plant has reached that point of general dissolution when the breakdowns are so continual that the loss of time and output occasioned thereby is too great a handicap to be overcome.

In every plant the expense of keeping the machinery in satisfactory working condition is taken care of by the current expenses, but very few plants have made any provision against the time when the entire plant must be rebuilt. Unquestionably, such a fund should be provided, or, in other words, if the plant is to be self-perpetuating, a fund should be set aside during the life of the plant for its replacement when it goes out of commission.

Most manufacturing enterprises frequently meet with extraordinary expenses, due to the breaking down of individual units. These breakdowns may come within a year or so of the starting up of a new plant, whereas the actual life of the plant itself may be many times this. If these expenses are allowed to come in the ordinary monthly cost sheets, these latter will show irregularities and will not serve so well as an indication of the operation of the plant during the period in which they occur; consequently it is desirable to have a certain fund available which can be used for such unit renewals.

These two funds, one for replacing units as they go out of commission and the other for rebuilding the entire plant, constitute the depreciation account. The former may be termed "current depreciation" and the latter "plant renewal depreciation." The former is to be used for the replacement of any individual units and the latter for the replacement of the entire plant.

To draw a parallel from the cement industry, let us take, for example, a cement kiln: this is a long, horizontal cylinder, revolving slowly on rollers and heated by a jet of pulverized coal or oil so that a temperature is maintained in it of about 2500° F. The lower part of the lining is subjected to the scorching action of the charge, and this part needs to be replaced about once a year. The cylinder itself, however, will last at least fifteen to twenty years. The replacement of the lining of the kiln should be taken care of by the current depreciation. There comes a time, however, when the outside shell of the kiln becomes worthless and when the entire apparatus must be replaced, and for this purpose we should be able to draw on a plant renewal fund. The proper plan, therefore, would be to estimate the average cost per year of repairing the lining and set aside a sum sufficient to cover this, crediting this sum to the current depreciation account. At the same time the life of the shell should be calculated and a sum sufficient to cover the replacement of this at the end of its usefulness should be set aside and credited to the plant renewal fund. In the purely chemical industries, the lead chamber offers an illustration of a piece of plant apparatus which must be replaced some day practically *in toto*.

Sometimes a machine is renewed part by part, as these wear out, so that at the end of a period of years there is probably, in its make-up, not one part originally present in the machine when it was first put on its foundations. Certain types of pulverizing machinery offer a good illustration of this. For example, with mills of the type of the Griffin and the Fuller-Lehigh mills, which are subject to constant repair, it is a fact that any of these mills which have been properly kept in repairs will be practically as good at the end of ten years' continuous operation as they were on the day on which they were installed. On the other hand, with the tube mill, for example, the cost of repairs is much lighter, but there will come a day when the entire mill must be replaced and the cost of such replacement will practically represent the cost of a new tube mill.

Depreciation of the value of a machine may also be caused

¹ Paper read at the Boston meeting of the American Institute of Chemical Engineers, June 27, 1913.

by the working out of other and more improved machines, by the discovery of a more economical process for the working out of the finished product from the raw materials in which this machine is not used, or even by the demand of the trade for a product that the original machine is not capable of producing. Such depreciation is now generally considered as a separate and distinct item known as "Obsolescence."

Where enlargement of the plant is made necessary by an increase in the demand of the product, this can be properly financed by increasing the capital if necessary. Such enlargements are in no way concerned with depreciation because for depreciation the original plant must actually depreciate in value. When new apparatus taking the place of the old has a greater capacity than the original apparatus part of the value of the former may properly be added to the capital account, but a part of it should certainly be taken care of by depreciation.

At the present time, competition in practically all industries is much keener than it was ten years ago and profits are much less. The introduction of the cost system has enabled manufacturers to determine accurately the factory cost of producing their goods, and many large manufacturers have been willing to undertake business using this system as a basis and figuring from this the prices of their product, allowing a fair return on the capital invested. As a result of this blind following of the cost system and the failure to take into consideration depreciation, etc., prices have often been figured far too low. It can be safely said that one of the first effects of keen competition has been to make manufacturers rely too closely upon the cost system in fixing prices. Ordinarily installed as a method of furthering the economic operation of the plant, it has of late years become the basis of prices themselves. Of course, the mill cost is an item in fixing the price at which a product may be sold but if a manufacturer considers only the cost of labor, fuel and supplies in making his prices he will sooner or later come to grief.

In many concerns, the failure to carry a depreciation account and the distribution in dividends to stockholders of money which should have been set aside for plant renewal has resulted in their ultimate financial distress.

Replacements are often made necessary by fire, floods, storms, explosions, etc. Such replacements can be properly made from the depreciation fund because new apparatus is installed and the opportunity can be taken to equip with improved forms of the latest design in place of the older type.

Obsolescence cannot be stated and figured so scientifically as depreciation. Certain things, however, can be borne in mind in considering this. Obsolescence, as a general thing, grows less as a process grows older. In every industry, the change and improvements which occur in its early years are much greater than those which occur later. Much of the obsolescence which has occurred to plants in the last few years has been due rather to need for greater outputs than to any actual efficiency of the earlier apparatus itself as compared with the later forms. In many industries, the general concession seems to be that plants have now reached the most economic size for a unit.

I might express my idea of obsolescence in the form of a curve in which one ordinate is the rate of obsolescence and the other time. Such a curve will take the form of a hyperbola. It is easy to conceive, however, that there may be a break in this curve due to some discovery which would revolutionize the art of manufacture in this industry. Such discoveries, however, have seldom been of such a nature as to put out of business old established concerns which could not adopt them immediately. Time is required to perfect the workings of a new process and most plants which are under competent management are informed of the discovery in sufficient time to make preparation for its adoption should it become universal.

As examples of radical changes in processes and the slowness

of the newer and theoretically much more efficient process to displace the older process, may be mentioned the electrolytic method for soda and the contact process for sulfuric acid. In spite of its apparent simplicity and marked advantages over the older methods, the electrolytic process for soda has not yet overtaken the older Solvay process. This latter process is fifty years old, and although it has now displaced the Le Blanc process to a great extent, it has required half a century in which to do it.

In the case of the contact process, the improvements in lead chamber practice seem to keep pace with the advances made in the operation of the former, so that ample time will be given manufacturers to change from the older process to the new should the latter prove to be the more efficient.

Most processes change detail by detail. Much apparatus in the old one could be used in the new; notably buildings, power plant equipment, conveying machinery, etc. The most radical change which could occur would probably be the substitution of a furnace process in place of a wet reaction one, or from a simple chemical process to an electrochemical one.

As an example of such a possible change, processes are being investigated at the present time for rendering available the phosphoric acid in phosphate rock by furnace methods. This, if successful and universally adopted, would decrease the consumption of sulfuric acid fifty per cent and cause the sulfuric acid plant, now a prominent part of many large fertilizer works, to become worthless and necessitate the installation of rotary kilns and pulverizing mills in its place.

The scarcity of labor might at any time cause machinery to become obsolete, owing to the need of replacing men by machines. In certain sections where labor is now cheap, it is easy to foresee conditions where an increase in wages might necessitate the entire reconstruction of a plant.

Obsolescence generally determines the value of the mill site since this is of course subject to no physical deterioration and is affected only by the need of moving the plant to a more advantageous site relative to climate, markets, raw materials, labor or transportation facilities. In certain industries, such, for example, as the manufacture of Portland cement, the extinction of the raw materials would affect the value of the mill site because when the raw materials are exhausted it will be necessary to move the plant to some other location. This form of obsolescence, however, can be calculated with the same degree of accuracy as depreciation.

How to handle depreciation best is a question which is open to considerable discussion. The ideal plan is unquestionably to set aside from the profits a certain sum each year. This amount should be derived by a very careful study of machinery and buildings and other appliances and assets of the company, including the patent rights. In every business, there are good years and bad years and it will be found, therefore, to be impracticable to set aside a fixed sum each year because there are times when even the most careful management will fail to make both ends meet, so that the good years must bear the heavy burden.

The depreciation account, as we have said, should be divided into two parts, one for use immediately and one as a reserve. The former should be used to repair breakdowns and make renewals of machinery of an extraordinary character and the latter for the renewal of the entire plant. The first is designed principally in order that the manufacturer's cost sheets may not vary too widely from month to month, owing to unusual repair items, and may serve as a reliable guide to the operation of the plant during various periods. In some industries, the repairs are small and the replacements are light, and in these, such a drawing account may not be necessary, but in most chemical, metallurgical and mining plants there should be set aside such a fund. There should also be set aside a sum representing the depre-

uation of the raw material deposits if there are any.

In plants which are financed entirely by the use of bonds, there is usually a clause in these latter which provide for a sinking fund sufficient to retire the bonds after a certain length of time. Plants which are financed in this way do not need a "plant renewal depreciation fund," because if their bonds have been retired, new securities can be issued and in this way sufficient funds may be raised to cover the cost of the plant renewal.

If depreciation is placed at too high a figure, manufacturers will be inclined not to consider it or, if they do, stockholders will be cut off from dividends which are rightfully theirs. The fact that the surplus is an asset of the company and consequently the value of its securities is increasing is not to be considered as answering this argument because many trust funds, etc., are invested with a view to bringing in steady revenues to the investors.

The question of depreciation is not simply one for the Board of Directors and the financial committee only. It is also a problem for the plant superintendent, the engineer, the chemist, and the geologist. It is only by a careful and scientific study of the subject that a proper figure can be arrived at. No two industries present the same conditions and probably no two plants manufacturing the same commodity will have the same life; hence depreciation is his particular problem with every manufacturer.

Obsolescence is always an unknown quantity and in a new industry it is much harder to gauge the rate of this than in an old one. Generally speaking, in most established industries the amount set aside for depreciation will also cover obsolescence.

Whenever the successful working of the plant is dependent upon a limited supply of raw materials, the life of the plant is fixed by the length of time the raw materials will last rather than by the wearing quality of the machinery. The depreciation fund in this case is, of course, the cost of replacing the plant and property.

As the first step in fixing the depreciation fund, the expert should consider the question of raw materials. If a local supply, how long will it last? Even if brought from a distance, the possibility of having to go still farther for it should be considered. Can new property be had at the cost of old? If the quality of the raw materials is decreasing, making it less easy to fashion the finished product as time goes on and possibly causing increased equipment, this should also be considered and provided for.

Next, the present equipment of the plant should be considered. Is it efficient and how soon will it have to be replaced? Is it already obsolete or does it represent present-day efficiency? Each piece of apparatus should be tabulated according to its probable life and value. Apparatus which needs to be replaced at the end of a year or so should be classed under the current renewal fund, and that with a longer life under the plant renewal fund.

From the plant renewal fund list should be excluded all apparatus which breaks down part by part, such, for example, as bucket-elevators, screw-conveyors, Griffin-mills and all small apparatus whose replacement represents a comparatively small sum, such, for example, as acid-eggs, cast iron evaporating pans, niter pots, etc.

Most apparatus has a salvage value even if sold only for its metal to the junk dealer. The amount of this may be calculated and deducted from the cost of new apparatus or it may be neglected altogether and considered merely as furnishing a margin of safety.

Let us take, for example, a cement plant of 3,000 bbls. daily capacity built, say, in the last year or two, and equipped with ball and tube mills for grinding the clinker and Fuller-Lehigh mills for grinding the raw materials, electrical drives, etc.

The capital raised for this will probably be distributed as follows

Plant and quarry equipment	\$1,000,000
Property	100,000
Office and laboratory	15,000
Working capital, bags, etc.	235,000
Cost of financing	150,000
Total	\$1,500,000

Let us consider the amount of raw material to be sufficient to last at least forty years. In considering the amount to be charged off for the extinction of the raw materials, the question is not merely one of present value but rather of the cost of replacing the property by a new one at the end of its usefulness. Since the life of the property is far greater than that of the plant, the latter will probably have been rebuilt several times before the extinction of the raw materials.

In the plant itself unquestionably much of the apparatus would have been replaced piece by piece in the course of current renewals.

The estimate of the cost of such a plant, showing the distribution, is given below:

COST OF BUILDINGS AND EQUIPMENT, 3,000 BBL. PER DAY PORTLAND CEMENT PLANT	
Buildings	\$200,000
Crushers, screens, etc.	25,000
Driers, coal and raw materials	25,000
Raw mills (Ball mills and Fuller mills)	70,000
Kiln and equipment	75,000
Coolers	20,000
Clinker mills (Ball and Tube mills)	75,000
Coal mills (Rolls and Fuller mills)	14,000
Elevators and conveyors	50,000
Bins and stock boxes	40,000
Shafting, pulleys and belting	20,000
Foundations, tunnels and concrete work	40,000
Power plant equipment	175,000
Motors	40,000
Wiring and electrical work	30,000
Machine shop, carpenter shop and blacksmith shop equipment	10,000
Miscellaneous equipment	41,000
Quarry equipment	30,000
Tracks, coal trestle and yards	20,000
	\$1,000,000

The above estimate includes the cost of installing the machinery and also its proportion of the engineering work, superintendence, clerical work, accident liability, insurance and other items incident to construction.

If the mill and kiln buildings are of steel, it would be safe to estimate their life, if properly painted and taken care of, at from forty to fifty years. Depreciation on steel mill buildings is usually considered at 2 to 2½ per cent. If the stone-house and the stock-house are of concrete with steel roof trusses, their life should be even longer. The roofs and sidings to the building would probably not have a longer life than fifteen to twenty years, so that the average life of the building could be safely placed at thirty years. It is hardly likely that they will become obsolete as modern machinery generally is more compact and, even if otherwise, steel buildings can be very readily enlarged.

No figures are obtainable upon the life of kilns. Some seven or eight years ago the size of the kiln was changed so that the long kilns now in use are none of them older than about ten years. These kilns do not show signs of going generally to pieces, although in some cases a lower section (25') may have to be riveted on. I think that 20 years would be a safe estimate of the life of an 8' × 125' kiln.

The driers and coolers are subject to considerable wear and tear—the latter particularly and the rotary coolers wear faster than the upright ones. The life of a stone drier on hard lime-

stone is generally about fifteen years and of a coal drier not over ten years. The crushers will last at least twenty years. Ball and tube mills should last this long also. Both, of course, need lining frequently. Griffin, Maxecon, Sturtevant, Hammer and Fuller mills are practically built over every few years. I think that with the ball and tube-mill installation 20 years would be liberal, as I know of mills still running efficiently which are nearly this old and which are probably good for many years more. The quarry equipment is subject to great wear and tear and I do not believe the life of steam shovels, cars and engines will be much more than ten years.

On engines, boilers and power plant equipment the figures generally used are from 5 to 6 $\frac{2}{3}$ per cent., or a life of from 16 to 20 years, and motors in cement plants, where they are subject to dust, cannot be expected to have much over 15 years of efficient life.

The bins and stock-boxes are quite an important item in the cost of a cement plant. These are not subject to appreciable wear and their life can safely be figured at 30 to 40 years. Furthermore, they are not subject to obsolescence and, in most plants with whose remodelling I have been connected, the bins in the old plant have been used in the new one.

Some of the concrete is in the foundations for the machinery and buildings and some of it in dams, retaining walls, tunnels, coal-trestles, etc., about the plant. Of itself, it is practically indestructible, but it is of course subject to obsolescence, particularly the foundations which may not suit the new machinery to be installed.

Machine shop tools are usually figured as having a life of 20 years, and accurate figures are obtainable on these. The tools in the cement plant machine shop are simple (lathe, drill-press, planer, etc.) and are not subject to very great obsolescence.

Wiring and electrical work, if substantially done, as it should be, if the figure given on the estimate is adhered to, may be safely assumed at the figures used by various electrical railroads, etc., for indoor wiring, *viz.*, 20 years.

Shafting, belting and pulleys will, for the most part, be taken care of by repairs, but these are also subject to obsolescence in that they may not suit new machinery.

Elevators and conveyors are subject to rapid wear and their renewal will come under repairs. The casings, metal troughs, etc., will have a long life, consequently they should be taken care of in the plant renewal fund.

The miscellaneous equipment is mostly made up of small items, many of which are subject to renewal as repairs, etc.

Rearranging the items in the above estimate of the cost of the plant according to their probable life, we see that in arriving at the proper figures for depreciation we must provide for \$80,000 at the end of 10 years, \$230,000 at the end of 15 years, \$277,500 at the end of 20 years, \$240,000 at the end of 30 years, and \$187,000 at the end of 40 years, when the raw materials become extinct. The latter sum includes the value of the office and laboratory. The amount to be set aside each year is found not by dividing \$80,000 by 10, etc., but by calculating the sum which, placed at compound interest, will net \$80,000 at the end of ten years. It is inconceivable that such a fund set aside each year would not bear interest. If invested in the business itself in the form of enlargements, etc., the depreciation fund should be credited by its earnings. A depreciation fund could be safely invested at 5 per cent interest and the interest so obtained reinvested with the new installments to the fund as they are set aside. So it seems perfectly proper in setting aside such a fund, to assume that it will bear compound interest for say at least 5 per cent.

A table calculated by Mr. John W. Hill, and first published in *Engineering News*, June 25, 1894, for calculating this sum, will be found in Kent's "Mechanical Engineers' Pocket Book," page 16.

PLANT COST ITEMS ARRANGED ACCORDING TO PROBABLE LIFE

Practically Indestructible			
Concrete work	\$40,000		\$40,000
10 Years			
Buildings	\$200,000		
Bins and stock boxes	40,000		\$240,000
20 Years			
Crushers, screens, etc.	\$25,000		
Kilns and equipment	75,000		
Clinker mills	75,000		
Raw ball mills	15,000		
Coal rolls	2,000		
Machine shop equipment	10,000		
Wiring and electrical work	30,000		
Shafting, pulleys and belting (25 per cent.)	5,000		
Elevators and conveyors (40 per cent.)	20,000		
Miscellaneous equipment (50 per cent.)	20,500		\$277,500
15 Years			
Power plant equipment	\$175,000		
Motors	40,000		
Stone driers	15,000		\$230,000
10 Years			
Coolers	\$20,000		
Coal driers	10,000		
Tracks	20,000		
Quarry equipment	30,000		80,000
Taken Care of by Current Renewal Fund			
Fuller mills	\$67,000		
Shafting, pulleys and belting (75 per cent.)	15,000		
Elevators and conveyors (60 per cent.)	30,000		
Miscellaneous equipment (50 per cent.)	20,500		132,500
			\$1,000,000

In the above case the sums to be set aside annually are as follows:

To provide \$80,000 in 10 years	\$6,360
To provide \$230,000 in 15 years	10,666
To provide \$277,000 in 20 years	8,392
To provide \$240,000 in 30 years	3,612
To provide \$187,000 in 40 years	1,548

Annual depreciation fund..... \$30,578

As the above plant will probably manufacture from 900,000 to 1,000,000 bbls. per year, this sum will be equivalent to from 3.01 to 3.4 cents per bbl. of cement produced.

On the extinction of the raw materials, two courses are open: either to retire entirely from business or to secure some other source of these and build a new plant at the new location. If the first course is followed, the depreciation should be increased by a sum sufficient to retire all of the securities at the end of forty years. The working capital at this time will most of it represent bills receivable and hence no provision need be made for retiring this. That portion represented by bags will probably be cut in half, but this will be offset in most cases by receipts from the sale of land, old machinery, buildings, etc.

The amount of depreciation to be fixed upon, therefore, in case plans are made to go out of business, will be the amount necessary to provide \$250,000 in forty years or an annuity of \$2,070, equivalent to from 0.23 to 0.21 cent per barrel, making the total depreciation in this event from 3.24 to 3.61 cents per bbl.

If new property is to be acquired, it is probable that this will be purchased as the opportunity presents itself to acquire desirable deposits of raw materials rather than at the expiration of the life of present holdings, and it is also probable that the transaction would be financed by the surplus profits of some period of good prices rather than by any fixed annuity.

In fixing a price for the cement, however, the cost of the raw materials, as represented by the purchase price of the property, should be included. Or considering the life of the deposit as

forty years, or 40,000,000 barrels, 0.25 cent should be added to the cost of production to cover the "in the ground value" of the raw materials.

In my estimation, the sum of 10 cents per barrel urged by some cement manufacturers recently is much too high. While it may be the part of wisdom to set aside some such sum as a "contingent fund," there seems to be no need of any such figure for depreciation alone.

202 N. CALVERT ST.
BALTIMORE

THE CORROSION OF LEAD¹

By RICHARD H. GAINES

The problem to determine what particular metal or combination of metals is best suited for a given purpose in engineering construction is sometimes one of great difficulty. A mistake in judgment may be at the expense of economy or durability or may even lead to a disaster. The decision of the engineer, to be correct, must be based on a thorough knowledge of the physical properties of the metals under consideration and this is generally gained by experience.

In many constructions, the choice of some of the materials is determined more by their durability under conditions of working than by their strength or other properties, a more expensive and weaker material being sometimes chosen in preference to a cheaper and stronger on account of superior resistance to corrosion. Examples of this are afforded by the frequent use of special bronzes in places where, except for their durability, the stronger and cheaper iron and steel would be preferable.

Incidental to a recent study to aid in determining whether it would be safe to substitute lead-lined steel pipe for bronze pipe where a material of great durability was required in portions of a water conduit, some experiments were made, and facts collected from the experience of others, bearing on the corrosion of lead. From the data obtained it was concluded that for the particular purpose in view, the relative merits of bronze pipe and lead-lined steel pipe would barely admit of comparison. Under whatever conditions lead withstands the action of water or acids, the bronzes are similarly unaffected, while under other conditions of service in which the bronzes are practically untouched by corrosive action, lead would be destroyed. Lead-lined steel pipes no doubt have their uses in the chemical manufactures, and may also find extensive application for the conveyance of hard waters, or acid waters of a certain character in mines, but they cannot be recommended for use in connection with city water supplies. Owing to its peculiar physical and chemical properties, lead affords a doubtful protection to iron or steel conduits from corrosion, and under some conditions might prove an absolute disadvantage if not an actual menace to the life of the pipe.

THE ACTION OF ALKALIES

A peculiarity of lead is that it may be corroded either by alkalies or acids. Thus, lime mortar, lime putty and lime water will attack lead; if the mortar is very alkaline the effect will be greater. Proof of this was established by experiment as well as from observation of lead service pipes in wet concrete.

The following experiment was made to test the effect of an alkaline seepage water on lead. A weighed sample of lead was immersed for a period of eight days in seepage water that leaked through the concrete walls of a tunnel. The sample was taken out daily, washed, dried and weighed, and the loss in weight noted. At the end of the test period, it was found that progressive corrosive action had taken place, amounting to 0.132 per cent in eight days, or at the rate of about 6 per cent a year.

Several examples of the corrosion of lead service pipes in wet concrete were observed, one of which it will suffice to men-

tion here. In a bathing establishment in Brooklyn two lead pipes passed up through a concrete floor—one of the pipes was for hot and the other for cold water. Owing to the free use of water on the floor the concrete was wet much of the time. Here the lead pipe for the conveyance of hot water was nearly destroyed by corrosion in five years, while the cold water pipe was also deeply corroded. No evidence was found of leaking electric currents in the building to aggravate this action.

CORROSION IN CONCRETE

A series of experiments was made to determine what loss lead suffers from corrosion as compared with steel, and some other metals when embedded alone, or in contact, in very damp concrete.

Specimens of the following metals were weighed and embedded singly and in contact in damp concrete and allowed to remain therein for two months. At the end of the test period the concrete blocks were broken up and the metals taken out, carefully cleaned, dried and reweighed, the loss in weight representing the amount of corrosive action in each specimen.

METALS:	SINGLE SPECIMENS		Loss	
	Grams Weight		in grams	
	Jan. 2, 1912	Mar. 4, 1912	Grams Loss 2 mo.	per sq. ft.
Manganese bronze.....	73.6655	73.6475	0.0180	0.32
Steel.....	39.1556	39.1481	0.0075	0.135
Lead.....	92.3806	91.7146	0.6660	11.99
Copper.....	73.7630	73.7272	0.0358	0.64
Monel metal.....	62.9667	62.9646	0.0021	0.04
METALS IN CONTACT				
Steel.....	37.0380	37.0270	0.0110	0.20
Manganese bronze.....	70.6864	70.6700	0.0164	0.30
Steel.....	38.1746	38.1700	0.0046	0.08
Lead.....	90.0399	89.5408	0.4991	9.08
Steel.....	38.8055	38.8031	0.0024	0.03
Copper.....	70.1913	70.1348	0.0565	1.04
Steel.....	38.6396	38.6271	0.0125	0.23
Monel metal.....	60.1092	60.1074	0.0018	0.30
Steel.....	34.5625	34.4626	0.0999	2.48
Lead.....	83.8596	83.5163	0.3433	6.77
Copper.....	68.9752	68.9626	0.0126	0.31
Steel.....	34.7072	34.8026	0.0676	1.68
Fiber.....
Copper.....	64.1247	64.1122	0.0125	0.31

The resulting losses show but slight differences when in contact and alone, and, therefore, give no evidence of electrolytic action when the metals are coupled in concrete. With the exception of the lead the corrosion loss of all the metals was small, that of the monel metal almost nil.

The action of the lead confirms results obtained from actual experience and shows that this metal may suffer very appreciably in an alkaline as well as acid medium. The corrosive action in this case was observed to be solvent in character, no protective coating being formed to hinder further change.

THE EFFECT OF ACIDS

Sir William Crookes once said that lead was the first cousin of thallium which Lothar Meyer called the ornithorhynchus of the metals. This strange jurassic animal, as some of you may know, possessed the body of a mammal and the beak of a bird. Whether such a doubtful order of relationship in the family of elements is true or not, it is a fact that the chemical properties of lead are very peculiar and they present some remarkable contrasts. While lead resists the action of sulfuric and hydrochloric acids in a far higher degree than iron, zinc or tin, it is readily attacked by weak organic acids and is slowly dissolved even by pure water.

With respect to corrosion the behavior of lead is decidedly inconsistent. Notwithstanding that lead is very slightly acted on by some of the strong mineral acids in the cold, it is soon extensively corroded when exposed to the action of moist air in the presence of carbonic acid and becomes eventually con-

¹ Paper presented before the New York Section of the American Chemical Society, Chemists' Club, May 9th, 1913

verted into a mass of white lead. Since carbonic acid is produced abundantly in the decay of animal and vegetable matter, metallic lead is much affected when kept in contact with such substances in the presence of air, the oxygen of which unites with lead to form an oxide which then combines with carbonic acid. The oldest process for the manufacture of white lead depends upon the corrosion of the lead by contact with decaying organic matter in this manner. Bloxam, in his work "Metals and their Properties," relates, "In breach loading cartridges where grease is employed as a lubricator, the bullets have sometimes become partly converted into white lead and thus increased so much in bulk as to burst open the copper case of the cartridges, and render it useless."

THE CORROSION OF LEAD IN THE SOIL

The impression prevails among many engineers that in the absence of stray currents, the corrosion of lead in the soil is negligible. This is not always true. While in some soils lead is very slowly affected by corrosion, in others an active chemical change or deterioration of one kind or another takes place; for example, "The lead of old coffins is sometimes found to have become almost entirely converted into an earthy-looking mass of basic carbonate of lead" (Bloxam, "Properties of Metals").

The Russian engineer, A. N. Schensnovitsch, of Odessa, recently sent by his government to New York to examine our pier and dock system, told the writer of an interesting case with which he was familiar of the destruction of lead water pipes by corrosion, that occurred in St. Petersburg during the seventies, before the days of industrial electricity or other conditions that could give rise to electrolysis. According to this engineer, in 1860-61, or thereabouts, a quarter of the city of St. Petersburg was served with water by a system of lead mains. In from ten to fifteen years these pipes had become so pitted by corrosion as to necessitate extensive changes. The cause of the trouble at the time was attributed to some local peculiarity of the soil, the exact nature of which was never ascertained. Mr. S. stated that the whole system was subsequently replaced by cast iron pipes, which had proved durable and satisfactory.

The superintendent of the water works of a suburban town in this vicinity told the writer that several years ago he had occasion to renew a number of lead service pipes on account of deterioration from corrosion. As he expressed it, "The pipes were pretty well used up, presenting the appearance of just having passed through a severe attack of small-pox. The lead moreover had the appearance of having lost all its vitality. There was no indication of electrolysis playing any part here."

In several cases reported by recent engineering periodicals, accounts are given of the lead pipe in the earth "losing its vitality, becoming brittle and porous, rendering renewal necessary after a comparatively short period of service, or the substitution of some other kind of pipe." Cases are also reported where it was deemed necessary to lay the lead pipe in wooden troughs, to surround it with pitch, or otherwise protect it from the corrosive influences of the soil.

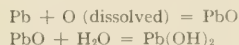
THE CORROSION OF LEAD IN WATER

So far as ordinary atmospheric corrosion is concerned, lead is one of the most durable of the common metals, undergoing no change in dry air or in water perfectly free from air. It is, moreover, but slightly affected by hard waters or dilute solutions of either hydrochloric or sulfuric acids. The latter acids quickly form coatings on the surface of the metal, which protect it from further action. Lead, however, is readily dissolved by water high in nitrates and by dilute nitric acid. It is also more or less rapidly corroded by weak organic acids in contact with moist air. Certain waters which actively corrode lead are those with a slightly acid reaction, from peaty swamps. There are certain microbes associated with peat which are acid-producing, and impart acidity to waters which have been in contact with peat.

Soft waters are particularly unsuited for conveyance in lead pipes, and in such waters containing nitrates derived from decaying vegetation, the amount of lead dissolved is large. Every plumber knows that pure soft water will attack, and sometimes destroy lead pipes. For this reason it has often been found necessary to line lead pipes with tin.

When lead pipes are acted on by water the corrosion is more or less irregular, some portions being hardly attacked, while at others, holes may be eaten through. This does not seem to be due to any irregularity in the metal, but rather to merely accidental circumstances. One authority quotes various experiments to show that lead water pipes should be kept full of water all the time to prevent deterioration.

The corrosion of lead by pure aerated water takes place as follows:



If exposed to the action of clean, soft water containing the normal quantity of dissolved oxygen, the lead is oxidized to hydroxide, which dissolves. After a time this is converted, by the action of the atmospheric carbon dioxide, into the basic carbonate of lead, $2\text{PbCO}_3, \text{Pb(OH)}_2$. Lead hydroxide is then again formed, and thus the corrosive action may be continued.

Potable waters always contain a certain amount of salts in solution, and the corrosive action depends to some extent upon the nature and quantity of the salts present. The waters which act least on lead are those containing carbonate of lime, phosphate of lime, and in a less degree, sulfate of lime. The waters which are most liable to act upon lead are those obtained from upland gathering grounds, waters which are soft and usually of remarkable purity. When highly oxygenated, the latter form no protective coating against solvent action. On account of the quantity that may be thus dissolved, lead has always been considered a more or less dangerous metal in connection with water supply for drinking purposes. Acting as a cumulative poison, its salts produce serious results if taken into the system even in very minute quantities for a length of time. Although indirectly related to the subject of corrosion, the experience of certain of the towns of Lancashire and Yorkshire in England should never be forgotten where the use of lead water pipes is under consideration. In these towns, lead poisoning was prevalent for a considerable period, doing immense damage to the health of the inhabitants before its real nature was recognized and its cause discovered. Incidentally it may be said that the compounds of lead are poisonous practically in proportion to their solubility. Thus the metal itself and its sulfide being incapable of absorption as such into the system, are practically innocuous, while the soluble salts, nitrate, chloride and acetate are active irritant poisons. The oxide, sulfate and carbonate are much less active, but continued exposure to lead fumes or to any atmosphere in which these substances are present in the form of dust brings on first "lead colic," and later, if exposure to the dust or fume is continued, a more chronic form of poisoning called "lead palsy" accompanied by great emaciation.

THE CORROSION OF LEAD BY ELECTROLYSIS

Instances are commonly reported of the electrolysis of lead pipes. In some of these cases, such as have occurred at St. Paul, Omaha and Paterson, N. J., all the phenomena of electrolysis were no doubt present. In others, damage from stray currents has by no means been proved, while the observed phenomena rather suggest ordinary chemical corrosion. In several cases of lead pipe deterioration called electrolysis, it was found that molecular changes of another character had taken place in the metal, similar to what Milton and Larke (Proc. Inst. C. E.) described as decay.

The electrolysis of either lead or lead-lined steel pipe, however, is a very real trouble, and the interest attaching to it here is the case with which it may occur and the rapidity with which

serious damage may be done. A few years ago the Westinghouse Electric Company showed by experiments at Pittsburgh how readily buried lead pipes could be corroded by electrolysis. This company also made a series of tests in different soils to compare the corrosive action of stray currents on embedded lead and steel pipes. It was demonstrated that in some soils lead pipes were even more rapidly destroyed by electrolysis than steel. This accords with actual experience reported from several cities. At St. Paul, where considerable damage to lead water pipe occurred, presumably from electrolysis due to escaping current from electric railway lines, cast iron pipes in the path of the same currents are said to have been little affected by corrosion. In New York City an engineer connected with the water department told the writer that in the few instances in which there had been any trouble from electrolysis of water pipes in Manhattan, "the lead joints were the first to go."

147 VARICK ST.
NEW YORK CITY

WOOD ALCOHOL¹

The comprehensive report on the chemistry, technology and pharmacology of methyl alcohol by Dr. Charles Baskerville, the issuance of which by the New York State Factory Investigating Commission is most opportune, owing to the prevailing hysteria regarding the use of wood alcohol and the need of reasonable changes in the present laws, is divided into the following sections:

Chapter I: "Wood Alcohol: What It is," Chapter II: "Manufacture of Wood Alcohol," Chapter III: "The Uses of Methyl Alcohol," Chapter IV: "Is Methyl Alcohol a Poison?" Chapter V: "Investigational Evidence and Recommendations;" Chapter VI: "Legislation Pertaining to Methyl Alcohol;" Chapter VII: "Conclusions and Recommendations;" Appendix A: "Affidavits of Employees as to Injury from Wood Alcohol Used as a Solvent for Shellac in Hat Stiffening;" Appendix B: "Free Alcohol;" Appendix C: I. "Summary of Cases of Poisoning by Drinking Wood Alcohol and Preparations Thereof;" II. "Summary of Cases of Poisoning by the Inhalation of Wood Alcohol;" and Appendix D: "Wood Alcohol Manufacturers in the United States."

THE GRADES OF WOOD ALCOHOL

The commercial wood alcohol on the market in 1896 was the same vile-smelling, greenish yellow, nauseous liquid as in 1850, and only quite recently was the deodorized product placed upon the market. Purified methyl alcohol is now sold under various names by American manufacturers, viz.: "Columbian Spirits," "Colonial Spirits," "Manhattan Spirits;" in Canada it appears under the names of "Green Wood Spirits" and "Standard Wood Spirits;" in Germany the newest variety is "Pro Spirit." The crude methyl alcohol of commerce is also termed wood spirit, wood naphtha, or pyroxylic spirit; it is a complex liquid, containing variable proportions of methyl alcohol, acetone, methyl acetate and formate, dimethyl-acetal, allyl alcohol, aldehyde, methylamine, oil, water, etc. The "tailings" contain furfural, methyl-ethyl ketone, and allyl acetate, with small quantities of paroxanthine. The best commercial wood spirit contains about 95 per cent or more of real methyl alcohol, the common varieties from 75 to 95 per cent, while some samples may contain only 35 to 40 per cent. The crude alcohol is a greenish yellow fluid, possessing a characteristic odor and nauseous taste; it is generally sold of a specific gravity of from 0.796 to 0.875 at 60° F. It is a good solvent and its

miscibility with water depends upon the amount of impurities present.

Dr. Baskerville indicates that methyl alcohol is contained in the steam distillates from a number of plants, in the fermented juice of fruit, and in the products of certain fermentations; and that methyl esters occur very frequently in volatile plant oils. He considers that these occurrences might require more than passing significance in chemically establishing the origin of wood alcohol in a matter of law, especially in connection with a question as to the presence of methyl alcohol in flavoring extracts and medicines intended for internal use.

THE MANUFACTURE OF WOOD ALCOHOL

The destructive distillation of wood is almost the only method of practical interest for obtaining methyl alcohol in the United States, although in Europe it is sometimes manufactured by the destructive distillation of peat¹ and also as a by-product from vinasse.² Methyl alcohol may also be prepared by a variety of synthetical reactions³ and recently a process has been developed for obtaining it as a by-product in the manufacture of wood-pulp by a soluble sulfite⁴ process.

The production from peat, vinasse and wood-pulp is considerable, and more or less incidental; and the synthetical methods are at present too expensive to be practiced on a commercial scale. The commercial demand for methyl alcohol is, therefore, essentially met by submitting wood to destructive distillation, the methyl alcohol, together with many other products, being obtained from the liquor condensed from the vapors evolved. The residue from the distillation is charcoal, which finds employment as a domestic fuel and in the smelting of various ores.⁵

The manufacture of methyl alcohol in the United States on a commercial scale is considered under the following heads:

A. The manufacture of the crude product.

- (1) The raw materials and their preparation.
- (2) The process of destructive distillation of the wood.
- (3) The separation and distillation of the crude product.

¹ For description of process, see W. A. G. von Heidenstam, *English Patent* 2,292, Feb. 5, 1900.

² Vinasse is the residue remaining after the distillation of fermented beet-root molasses.

³ The chief methods proposed are:

A. From methane: (1) By chlorination in reflected sunlight (Berthelot, *Compt. rend.*, **45**, 916); (2) Incomplete oxidation (Maurin, *Bull. soc. chim.*, [2] **19**, 243); (3) Oxidation with ozone at ordinary temperatures (Otto, *Ann. chim. phys.*, [7] **13**, 77); (4) By passing methane and air over finely-divided copper (Glock, *Ger. Pat.* 109,014 of 1898; Coquillon, *Z. Spiritalind.*, **23**, 182); (5) By oxidation with hydrogen peroxide, ferrous sulfate, monopersulfuric acid, combined or alone (Lance and Elworthy, *Eng. Pat.* 7,297, March 26, 1906); (6) By oxidation at 30–50° C., using tan bark as a contact substance (Hausmann & Co., *Ger. Pat.* 214,155, Sept. 26, 1906).

B. By the dry distillation of calcium formate (Lieben and Rossi, *Gaz. chim. ital.*, **1871**, 164; Lieben and Paterno, *Ann.*, **187**, 293; Friedel and Silvia, *Bull. soc. chim.*, [2] **19**, 481).

C. By the electrolysis of an organic salt: (1) From potassium malonate (Peterson, *Z. phys. Chem.*, **33**, 714); (2) From potassium acetate (Hoefler and Moest, *Z. Elektrochem.*, **10**, 833); (3) From sodium acetate, perchlorate, sulfate and potassium carbonate and bicarbonate (Moest, *Chem. Centr.*, **74**, 1, 370).

D. From formaldehyde: (1) By the action of potassium hydroxide (Lieben, *Monatsh.*, **22**, 302); (2) By the action of light on a mixture of it with water (Inghilleri, *Z. physiol. Chem.*, **73**, 144).

E. From glycerine and glycerates: (1) By distillation of glycerine with soda (Fernbach, *Bull. soc. chim.*, [2] **34**, 146); (2) By the action of carbon dioxide on sodium glycerate at 180° C. (Loebisch and Loos, *Wein. Anz.*, **1881**, 252).

F. From prussic acid (Linnemann and Siersch, *Chem. Centr.*, **39**, 390).

G. From acetone by saturation with hydriodic acid or hydrochloric acid (Friedel, *Compt. rend.*, **46**, 1165).

H. By the action of a zinc salt [Zn(C₂H₃)₂] upon monochlor-ether (Henry, *Chem. Centr.*, **62**, II, 680).

⁴ See Meyer, U. S. Pat. 407,422, July 23, 1889; Stora Kopparbergs Bergslags Aktiebad, French Pat. 402,331, April 23, 1909; Bergstrom, *Papier-fabrikan*, **8**, 970.

⁵ Chiefly iron ores, for the production of Swedish pig-iron.

¹ Abstracted from "Wood Alcohol: A Report on the Chemistry, Technology and Pharmacology of and the Legislation Pertaining to Methyl Alcohol," prepared for the New York State Factory Investigating Commission by Dr. Charles Baskerville, Professor of Chemistry and Director of the Laboratory in The College of the City of New York, and Chairman of the Committee on Occupational Diseases, American Chemical Society.

B. The refining of the crude product. Purification and rectification, especially the separation of the acetone.

Hard woods, preferably birch, beech, maple, oak, elm, and alder, are best for the purpose, and recently processes have been developed for the destructive distillation of sawdust and wood-waste.¹

The wood used is thoroughly seasoned for 1 to 2 years and cut in 50-inch lengths.²

The destructive distillation is carried on in large iron retorts at a temperature³ of 400–500° F. These retorts are usually made of steel of varying dimensions, and are provided with large, tightly fitting doors, and are also provided with outlet pipes about 15 inches in diameter, or the gasified products may be taken out through several delivery tubes on the side of each oven. The retorts are set in pairs in brickwork and batteries of from 2 to 20 pairs are common. The cord wood is fed through the door and carefully stacked so as to completely fill the retort, or steel cars are loaded with the wood and run into the retort. In the larger works the retorts are constructed of brick and are of 50 cords capacity. They are provided with heavy iron doors, which may be sealed after opening. The doors are tightly closed and the retorts are heated from below by burning wood, coal, or charcoal, supplemented by the tar, red oil, and gas which are by-products in the industry, or the ovens may be heated by burning natural gas.

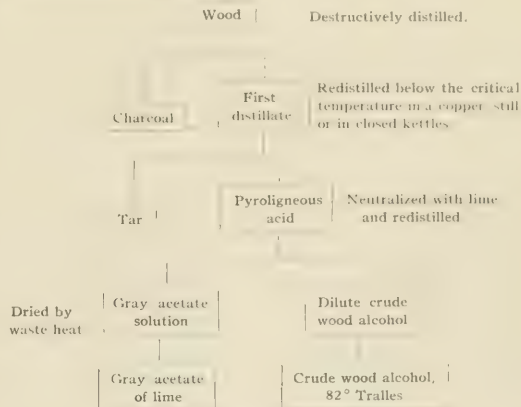
The gasified products of the distillation are run through condensers. The non-condensed gaseous products are returned and burned under the retorts.

The products condensed are run into tanks, and the tar is allowed to settle out; the pyroigneous acid containing acetic acid, methyl alcohol, acetone, allyl alcohol, phenols, etc., remains on top. The pyroigneous acid is a dark red-brown liquid, having a strong acid reaction and a peculiar empyreumatic odor; its density varies from 1.02 to 1.05. It is used to a limited extent in the manufacture of an impure acetate of iron, known as "black iron liquor" or "pyrolignite of iron," but is usually treated to separate the methyl alcohol (of which it contains about 4 per cent.), acetone, and acetic acid. This is done by fractional distillation. The acetic acid is recovered by passing the vapors through milk of lime, whereby "gray acetate of lime" is obtained, or the pyroigneous acid is neutralized with lime before distilling off the alcohol, which latter process is technically called "making a tub." Usually three stills of about 2500 gallons each are employed and from them are obtained distillates containing 15, 42 and 82 per cent wood alcohol, respectively. It is a closed process, but not necessarily a continuous one. The commercial product thus obtained is of 82 per cent strength by the Tralles alcoholometer, and contains varying amounts of acetone and other substances.

A graphic presentation of the process is shown in the accompanying diagram.

This crude material is usually shipped to a centrally located refinery in tank cars, iron drums, or in barrels, for purification and rectification. This is accomplished by further distillation from lime or caustic alkalis. The acetone cannot be removed by simple distillation and various methods for its separation have been proposed, viz.: conversion into chloracetones of high boiling points; conversion into chloroform and volatilizing by distilling the mixture with chloride of lime; crystallizing the methyl alcohol with calcium chloride and separating; forming the methyl ester, separating, decomposing by caustic potash

and obtaining the alcohol by distillation. Various types of rectifiers are used. The final product thus obtained is commercial wood alcohol, which is usually sold at 95 per cent strength by Tralles' alcoholometer, but may contain from 10 per cent to 20 per cent acetone and varying proportions of other organic impurities. Sometimes commercial wood alcohol is still more highly rectified and refined up to strengths of from 97 to 98 per cent by volume of real methyl alcohol, and is then sold under various trade names.



THE EXTENT OF THE INDUSTRY

The manufacture of acetate of lime and methyl alcohol was started in the United States about 1867, by James A. Emmons and S. A. Saxon, of Crawford County, Pa., although the manufacture of pyroigneous acid was begun by Ward at North Adams, Mass., in 1830. In 1874, George C. Edwards established the Burcey Chemical Works at Binghamton, N. Y., to refine the crude wood spirit produced by various manufacturers. In 1900, there were 99 establishments in the United States producing some of the crude substances enumerated above; of these, 84 were regular wood-distilling establishments, and produced 4,191,379 gallons of crude alcohol, having a value of \$1,660,061; 81,702,000 pounds of acetate of lime, having a value of \$926,358; and 14,428,182 bushels of charcoal, having a value of \$612,009. These works employed \$4,858,824 of capital and 1,268 wage earners. There were nine establishments reporting the production of the crude material and the refining of the alcohol in the same factory; and these establishments produced 637,856 gallons of refined alcohol, having a value of \$370,513; 5,134,000 pounds of acetate of lime, having a value of \$34,928; and 2,726,120 bushels of charcoal, having a value of \$114,663. They employed \$760,150 of capital and 254 wage earners. During the years 1909–10 there were 147 establishments engaged in wood distillation in the United States, employing 3,039 wage earners and \$13,017,000 of capital. Of these, 117 were engaged in wood distillation of hardwoods, chiefly birch, beech, and maple. The quantity of hardwood consumed during the year was 1,257,997 cords, or 86.7 per cent of the total of all woods consumed in distillation, and the total value of the product was \$9,737,000.

At the present time there are 63 manufacturers of wood alcohol in the United States.

The larger part of the export of wood alcohol for the past six years went to Germany, the United Kingdom, and Belgium. During 1910, wood alcohol valued at \$5,696 was imported into the United States.

Among the European nations, Austria Hungary and Sweden are large producers of crude wood spirit, while Germany is the principal marketer of purified wood spirit. The crude wood

¹ See Bergman, U. S. Pat. 504,264, Aug. 29, 1893; Fischer, *Z. anorg. Chem.*, **1900**, 192; Oregjaevac, *Chem. Fabrik. Muller*, French Patent 457,432, Sept. 2, 1905; Walker, *J. Soc. Chem. Ind.*, **30**, 934; Norton, U. S. Consular Rep., Nov., 1911; *Chem. Eng.*, **16**, 1.

² In most distillation plants, the wood is divested of its bark.

³ No decomposition occurs below 160° C.; between 160–275° C., the pyroigneous acid is formed; about 275° C., the yield of gaseous products becomes marked; between 350–450° C., liquid and solid hydrocarbons are formed; and above 450° C. little change occurs.

CRUDE MATERIALS PRODUCED, 1880 TO 1910

Year	No. of establishments	Wood alcohol		Acetate of lime		Charcoal	
		Gallons	Value	Pounds	Value	Bushels	Value
1880	17	.	\$86,274	6,893,009	\$186,892		\$31,770
1890	83	1,116,075	688,764	26,778,415	315,430		
1900	93	4,948,963	1,976,986	86,876,000	981,286	17,154,302	726,672
1910	147	8,468,083	2,582,253	170,000,000	3,600,000	42,000,000	2,700,000

EXPORTATION OF WOOD ALCOHOL, 1900 TO 1911

Year	Gallons	Value
1900	540,799	\$320,306
1904	1,194,466	585,359
1905	1,097,451	603,385
1906	780,222	466,467
1907	2,150,311	862,819
1908	1,958,630	819,753
1909	1,100,495	383,788
1910	1,691,000	760,000
1911	2,040,000	898,000

spirit imported into Germany in 1911 amounted to 8,759,300 kg., valued at 5,694,000 marks: 4,168,700 kg. came from Austria-Hungary, 268,700 kg. from Sweden, and 4,318,800 kg. from the United States. In 1910, 8,726,900 kg. of crude wood spirit were imported. In 1911, Germany exported 1,739,200 kg. of purified wood spirit, valued at 1,267,000 marks. France took 919,300 kg., Italy 138,700 kg., Holland 236,300 kg., and Switzerland 170,500 kg. In 1910, 1,782,400 kg. of purified wood spirit were exported by Germany. In 1910, France imported methyl alcohol valued at 1,819,006 francs, while the exportations for the same year were valued at 106,480 francs. In 1911, 291,600 kg. of methyl alcohol, valued at 379,080 lira, were imported by Italy, while but 500 kg., valued at 650 lira, were exported.

THE USES OF METHYL ALCOHOL.

A. For Denaturing Ethyl Alcohol.¹

B. In the Chemical Industries.

The chief uses of wood alcohol in the chemical industries are as follows: (1) As a solvent; (2) as an extraction agent; (3) as a raw material for the production of formaldehyde; (4) in syn-

¹ Denatured alcohol is employed in large quantities in the arts and crafts and in the chemical industries; and in recent years it has displaced wood alcohol to a large extent. It is used as a solvent for shellac in the manufacture of all kinds of wood products, such as passenger cars, carriages, furniture, pianos, organs, billiard tables, burial caskets, toys, whips, trunks, pipes, etc. Shellac is used as a binding material in the manufacture of lead pencils and electric motors and generators. It enters intimately into the manufacture of stiff, silk, straw and felt hats, in which cases the shellac is incorporated in the body of the hat by the aid of alcohol. Similarly, it enters into the manufacture of lacquers, enamels, etc., used to enamel the surface of metals such as hardware, iron, brass beds, gas and electric fixtures, lamps, brass musical instruments, bird cages, clocks, watches, toys, etc.

The manufacture of celluloid, xylonite, artificial silk, collodion, etc., are dependent upon the availability of denatured alcohol. It is used in large quantities in the manufacture of smokeless powder, fulminate of mercury, and other explosives. An important use of industrial alcohol is in the manufacture of ethyl ether and ethyl chloride. Another utility of the alcohol is in the production of dyes, where it enters as a solvent, a medium of interaction, or as a chemically active body. There is also the manufacture of fine chemicals, a very important industry in which alcohol enters.

The use of denatured alcohol as an illuminant, fuel and in gas engines is of growing importance. Hundreds of patents have been granted for all sorts of alcohol lamps, and numerous alcohol heating mechanisms have been put on the market, especially in Europe.

The withdrawals of alcohol in the United States in the fiscal year 1910-11, for the purpose of denaturing, upon which no taxes were paid, amounted to 11,062,060 proof gallons, and there remained at the end of the year, in bonded warehouses, 2,213,390 proof gallons. In 1910-11, Germany produced 91,765,078 gallons of alcohol, of which 37,141,633 gallons were consumed in the industrial arts; and in 1910, 3,962,412 gallons of denatured alcohol were made in England. The Swiss importations of denatured spirit amounted to 6,993,900 kg. in 1911; of this quantity 6,246,500 kg. came from Austria-Hungary, a large producer of methyl alcohol.

thetic chemistry for the introduction of the methyl (CH_3) group; and (5) as a reagent in chemical laboratories.

(1) Wood alcohol is a good solvent for fats, volatile oils, camphor, resins, gums, alkalies, and various salts. Because of its cheapness, it is used as a solvent for varnishes, lacquers, stains, finish, and shellac. It is also used as a solvent in the manufacture of certain inks, photographic materials, celluloid, xylonite, and similar products, and incidentally in the manufacture of transparent soap. In celluloid, xylonite, etc., the alcohol does not appear in the finished product, while in varnish, shellac, etc., the wood alcohol remains as such and may produce its deleterious effects on workmen employing these in the industries.

(2) As an extractive, wood alcohol is used in the manufacture of smokeless powder, fulminate of mercury, nitrocellulose, and other explosives. Thus, dried, pulped military guncotton is freed from lower cellulose nitrates by extraction with wood alcohol.

(3) Formaldehyde, which has an extensive use, is produced from methyl alcohol by oxidizing with air by the aid of a catalytic agent. It is prepared on a large scale by passing a mixture of methyl alcohol vapor and air over a glowing platinum spiral or heated copper gauze. Formaldehyde may also be prepared by the electrolysis of dilute methyl alcohol and when ozone is passed through it. Commercial formaldehyde is a 40 per cent water solution, containing from 12-15 per cent of methyl alcohol.

(4) Methyl alcohol is used in synthetic chemistry for the introduction of the methyl group (CH_3) into various substances. In the manufacture of artificial perfumes and flavors, it was discovered that the presence or addition of the methyl group converted certain odorless and tasteless bodies into those possessing strong perfumes or flavors. Thus, methyl benzoate ($\text{C}_6\text{H}_5\text{-COOCH}_3$) is prepared by distilling wood spirit with benzoic acid and sulfuric acid; it is used in perfumery, under the names "Essence Niobé" and "Peau d'Espagne." Methyl beta-naphtholate ($\text{CH}_3\text{O.C}_{10}\text{H}_7$), known in commerce under the names "Nerolin" and "Yara-yara," is prepared by boiling beta-naphthol with methyl alcohol and zinc chloride; it is one of the strongest smelling perfume materials. Methyl cinnamate ($\text{C}_6\text{H}_5\text{CH:CH.COOCH}_3$) is prepared by distilling methyl alcohol with sodium cinnamate and sulfuric acid; it is used as a flavoring extract in confectionery and as a perfume. Methyl anthranilate, a very fragrant perfume, is prepared by condensing anthranilic acid with methyl alcohol. Methyl alcohol is also used in the preparation of vanillin, etc. It is used in a similar manner in the manufacture of various aniline dyes, viz., methylene blue, green, and violet.

(5) Methyl alcohol is used as a reagent in chemical laboratories for the detection of salicylic acid, the determination of boric acid, in the preparation of grape-sugar, and as a substitute for ethyl alcohol for various purposes.

C. In Pharmaceutical and Medicinal Preparations.

Methyl alcohol is employed in the preparation of synthetic drugs (methylal, methyl esters, etc.); solid medicinal preparations, surgical dressings, cattle medicines, plant washes, and in capsules and other medicinal appliances improperly in toilet preparations (bay rum, witch hazel, "Florida water," etc.), and in essences, extracts (extract of lemon, orange, etc.), tinctures (tincture of iodine, etc.), liniments, lotions and embrocations, patent medicines, proprietary and domestic medicines.

D. In the Arts and Crafts.

Methyl alcohol finds application as a solvent in the manufacture of hats (stiff, silk and straw), electrical apparatus, gas and electric fixtures, furniture, pianos and organs, cabinet work, picture molding, burial caskets, passenger cars, wagons and other vehicles, boots and shoes, toys, whips, lead pencils, brushes, rattan goods, brass beds, various kinds of metal hardware, incandescent mantles, artificial flowers; in dyeing establishments; in cleaning in laundries, etc., and in the painting industry.

E. Unclassified.

Other uses of methyl alcohol are as a fuel and illuminant. It is also employed for a variety of domestic purposes (cleaning, etc.).

THE ABUSES OF METHYL ALCOHOL

The data collected by Dr. Baskerville indicate that the drinking of liquors containing methyl alcohol is responsible for most of the deaths and blindness attributable to methyl alcohol. The "deodorized" methyl alcohol resembles ethyl alcohol so closely that the ordinary layman can hardly distinguish the difference between the two, and, as it costs less than one-fourth as much as grain alcohol, people are tempted to use it as a substitute for ethyl alcohol in adulterating whiskey, essences, extracts, bitters, washes, liniments, balsams, perfumes, etc. The victims are generally those who indulge in the commoner forms of whiskey, rum and wine, although persons not addicted to the use of intoxicating drinks are undoubtedly often affected innocently, from drinking Jamaica ginger, lemon extract, essences, bitters, medicines, etc., whose chief menstruum is "deodorized" wood alcohol. Happily these abuses are growing less through the operation of the National Pure Food and Drugs Act of June, 1906.

THE POISONOUS NATURE OF METHYL ALCOHOL

After critically reviewing the ideas which have prevailed at various periods regarding the toxicity of methyl alcohol and the investigations which have been conducted on this point, Dr. Baskerville is led to conclude that methyl alcohol is less poisonous to lower plants and infusoria than ethyl alcohol, but for higher animals, and especially for man, it is a severe toxic agent. Its poisonous properties are doubtless due, first, to a specific action, and then to its oxidation in the body, first to formaldehyde and then to formic acid. It is furthermore a cumulative poison. It produces toxic effects whether it is taken internally or inhaled through the lungs.

It is a matter of little practical importance, he continues, as to whether *chemically pure* methyl alcohol is toxic or not, as economic reasons prohibit its extended use in the arts and manufacturing industries, although the purest material is used in certain products. The numerous cases of poisoning prove beyond doubt that the methyl alcohol of commerce is decidedly toxic.

CONCLUSIONS AND RECOMMENDATIONS

After a consideration of the published cases of poisoning by the use of methyl alcohol (a summary of these is given); the evidence which has been presented by experts, physicians, manufacturers and workmen as to the injurious action of wood alcohol when drunk, inhaled, or used externally; the recommendations which have at various times been made by individual experts and organizations to limit the sale and use of methyl alcohol; and the legislation, both in the United States and in foreign countries pertaining to methyl alcohol, Dr. Baskerville arrives at the following conclusions:

1. (a) While there may be differences in opinion as to the actual toxicity of absolutely pure methyl alcohol, the preponderating evidence indicates that its physiological action spells injury. The toxicity of the ordinary methyl alcohol of commerce, commonly called wood alcohol, even though it be of a higher

grade of purity, is a recognized fact, whether its morbid action is due to the concomitant impurities or not.

The use of methyl or wood alcohol in any food, condiment, flavoring extract, or liquid capable of being used in whole or partially as a beverage, or internally as a medicine, should therefore be prohibited by law. This is covered in part at present by Article 8, Agricultural Law 201, 1909, State of New York.¹

(b) In connection with the New York law, attention is directed to a lack in clarity, and, in consequence, likely in justice from attempts at its execution. The use of the word "methylated" is ambiguous. In the loose English sense it means ethyl alcohol which has been denatured with methyl alcohol, but it has an even wider meaning from what might appear as its real intent. One instance is cited to illustrate the point. Methyl salicylate, oil of wintergreen, is a recognized product of manufacture used for flavoring, which is a "methylated" preparation. It is identical with oil of wintergreen prepared from natural sources. If the synthetic preparation were properly labelled, it would not be a case of misbranding, morally, within the meaning of the section,² yet a court could very properly hold that it was, because synthetic oil of wintergreen is a "methylated preparation." The wood alcohol is no longer present as such and the physiological action of the wood alcohol is no longer observed. The above is true of many synthetic perfumes, flavoring extracts, and drugs of recognized medicinal value which are welcomed as legitimate commercial products of the chemist's art.

2. Wood alcohol should not be permitted in preparations such as perfumes, witch hazel, bay rum, eau de cologne, liniments, washes, etc., which are intended primarily for external use on the human body. It is remarked that "tippling" with these preparations is not uncommon.

The question of allowing ethyl alcohol which has been denatured with methyl alcohol to be used for this purpose, namely, in liniments, etc., might appear as one open to argument primarily on the basis of dilution. The denaturing formulas now in effect by Federal consent do not encourage but discourage the use of industrial alcohol for such purposes. The opinion is expressed that it would be better to err on the safe side and to make the restriction only as the occasion arises.

3. In the manufacture of wood alcohol the workmen are liable to come into contact with the vapor only in neutralizing the acetic liquor with lime and in filling the shipping containers. In the case of the former, the common practice now is to carry out the operation in closed vats which are opened only when the lime is added. General requirements for *ample ventilation* should meet these difficulties, which, in fact, do not now exist in the works inspected in New York State.

4. Wood alcohol is a valuable solvent used as such extensively in the arts in two important ways:

(a) It is used as a solvent in the *course of the manufacture* of many substances, but does not appear in the product when the latter is put upon the market. It is not destroyed but evaporates or is saved in part by condensation. It can exert its deleterious action during the process

- (1) by the workmen inhaling its vapor,
- (2) by the workmen constantly dipping their hands and arms into the liquor, or
- (3) by the workmen drinking the wood alcohol.

Ample ventilation will meet the first difficulty. Standards

¹ This article is as follows: "200. No person, firm, association or corporation shall, within this state, manufacture, produce, sell, offer or expose for sale any article of food which is misbranded within the meaning of this article."

² "201. Definition of adulterated or misbranded food. An article of food shall be deemed to be adulterated if it contains methyl or wood alcohol, in any of its forms, or any methylated preparation made from it."

³ No. 200, loc. cit.

should be determined in each case by the Board of Health or such board with authority as may be designated.

In the second case the workmen should be provided with impervious long gloves or the processes should be operated mechanically; if a closed process is used, the first difficulty is also largely met.

Education only can solve the third problem.

(b) Wood alcohol serves as a solvent or menstruum of the material which is placed on the market in a liquid form (varnishes) and exerts its action upon the users, depending upon multimform conditions. In works where these materials are used in large quantities and the solvent evaporates, *ample ventilation* should be required. In many cases, however, the workmen are more or less isolated. They may and should be warned of the danger attendant by suitable labels on the vessels containing the liquid they are to apply.

5. All bottles or vessels used for transporting or selling products containing wood alcohol should be required to bear a prominent display label stating that it contains a "Poison."

RECOMMENDATIONS AS TO LAWS

The existence of the following laws is recommended:

1. A law prohibiting the presence of wood alcohol in any form of material intended for internal use.

2. A law prohibiting the presence of wood alcohol in preparations intended for external use on the human body.

3. A law requiring *ample ventilation* in works where wood alcohol is made or used in manufacturing products wherein the wood alcohol remains as such; the same law should apply where the products containing wood alcohol are used up, as, for example, in varnishing vats in breweries.

4. A law requiring containers in which wood alcohol is marketed to bear suitable display labels of warning.

These laws should be so drawn as not to inhibit use of wood alcohol in manufacturing products in which methyl alcohol supplies a constituent part, but does not remain as wood alcohol therein.

SOME PECULIAR FUNCTIONS OF THE RETAINED EXPERT¹

By W. M. GROSVENOR

One dislikes to use the name "expert" for three excellent reasons. It is as much abused by careless use as the name lady—likewise most applied where it least belongs. It savors of a holier-than-thou snobbery that is obnoxious to the plain common sense that recognizes every man as expert in some direction, from ditch digging to diplomacy. Finally, in the legal sense experts have sometimes taken advantage of their peculiar position as opinion witnesses to a sinister extent. An illustration from the files of the patent office is not without interest. In the early days of telegraphy an application was filed for a new kind of relay that, to make it very sensitive, possessed a long arm pivoted near one end between strong electromagnets and making relay contacts at the other. The examiner found nothing to anticipate it, but wrote the applicant to know, before allowing the application, why it was entitled "Expert Relay." The applicant answered that he called it a relay because it was for repeating forward telegraphic impulses and an expert because it possessed a tongue suspended in the middle and adapted to lie with equal facility in either direction according to the nature of the influence brought to bear.

This, however, is not the peculiar function of the expert that I desire to present. Aside from the so-called "expert" notorious chiefly for holding to one opinion or avoiding another, there is the real expert in getting, marshalling and using facts—sometimes quite tangible facts, like the type of man nature made him, but natural selection draws the narrower specialist into the employ of some one company or plant and further narrows

him, while selection likewise urges the broader (sometimes shallower) man into general consultation work that further broadens his activity and experience until the particular science in which he was especially trained becomes but a subordinate part of his activity. It is the latter expert that interests us at the moment. To avoid the word "expert" I suggest we call him a *retainer*—a perfectly good English word implying honorable and somewhat independent service and loyalty.

For such work I believe chemical engineers to be peculiarly fitted, judging by the number who have succeeded in this field. Nor is this surprising when we consider that a general knowledge of Chemistry to-day begins at the very foundation of matter and energy and of necessity involves the fundamentals of mathematics, physics, mineralogy and biology, that as engineers by training or adoption the practical development of all this theory has been made compulsory and that all of this work has been done with the insight and thorough understanding that the chemical type of mind induces.

We read these days of scientific detectives—some fiction—but there is a sufficient basis of scientific fact to satisfy certain dynamiters. The scientific detective has certainly arrived and is making good. What I wish to point out and then to illustrate by a few examples is that the *retainer* has practically the same functions for industrial life and uses practically the same weapons as the scientific detective. It is his privilege to foresee and prevent, or to detect and penalize the industrial waste, deceit, misrepresentation, infringement, and forced bankruptcy that correspond to loss, fraud, blackmail, theft and murder in commercial and social life. Likewise his chief weapons are common sense, patience and experience and to him no knowledge comes amiss. Both men are detectors of fact guided by combined theory and experience and must check up by experiment or test.

Whatever the employer's problem, the *retainer* can bring to its solution two invaluable contributions: *first*, the independent, impersonal point of view of one neither involved in the petty detail of the business nor prejudiced by preconceived ideas or parental relation to the matter; *second*, a broad experience with different managements and ways of getting results, different plants and different branches of industry. If it is also true, as of the Italian bandit, "He had studied human nature and he knew a thing or two," he can be almost invaluable to his employer—and quite valuable to himself. To illustrate:

A *retainer* was faced with a problem of daily hoisting 3,000 tons of sulfuric acid about 80 ft., and because he had not grown up with the problem but met it fresh with other things in mind, he cut the usual cost down 60 per cent by putting in a balanced pair of ten-ton mine skips.

Another *retainer* without special foundry or crane experience was asked to reduce the excessive number of accidents in one foundry handling a large number of very heavy castings; he studied the problem a few days and concluded it was a matter of temperament; that the crane men were casually selected from the mechanical force predominating in nervous or energetic rather than cautious men. A new gang was carefully selected for cautious combativeness from various points in the plant and before trying them out the duties and dangers were carefully explained. So well were they selected that all the first lot threw up the new job before trying it. Another lot with milder explanation took over the cranes and the accidents ceased almost immediately.

A new type of shellac drier had just been installed and tested. It reduced the drying time from 48 hours to 3 hours and the floor space from 6000 square feet to 200 square feet, but the shellac packed and gradually built up on the sides of the drier, making no end of trouble. The *retainer* of the drier company, who knew nothing about shellac and had not heard of this particular drier, was sent for, looked the drier over, felt of the shellac

¹ Paper read at the Boston Meeting of the American Institute of Chemical Engineers, June 25-28, 1913.

to be dried and in various stages of dryness by the old process, made a short preliminary test, and then ordered the circuit opened for the first hour of each three-hour treatment to reduce the initial humidity. The packing promptly ceased.

A northern manufacturer of muriatic acid called up on the phone to say that his plant was crazy. It took in raw material but did not produce acid, so the absorption water grew weaker and had to be shut off. The retainer knew the plant, instructed pressure tests with a draft gauge to be made at certain points, and reported by phone. When the report came in he asked, "How was the weather last night?" "Bitter cold," came the answer. "Thaw out the crystalline hydrochloric hydrate from your air precooler with warm water," was the advice.

A certain man was retained by one of the textile coating firms and after making his first trip through the plant asked for the largest single items of expense for material not actually present in the finished goods. Volatile solvents used with the coating material were first mentioned to the amount of \$400 a day. In reply to his question why this was not recovered it was stated that this had been tried elsewhere and failed for two reasons, *i. e.*, only 30 per cent recovery had been made but, far more important, the quality of the goods had been injured. He offered reasons why the tests must have been carried out under improper conditions to show such results, and advised testing again. He condenses two years' development into a sentence and says, "The first little test box showed 50 per cent recovery and improved the quality of goods, and the commercial installation on formal test showed 80 per cent recovery, better quality and 25 per cent reduction in labor for the operation."

A large garage company desired to improve their competitive position and sought advice. On examination, no chance for considerable improvement appeared until petrol sales were examined and found to be a source of considerable revenue and a possible drawing card if the petrol were treated and carefully clarified. A special high-grade petrol was made a great talking point thereafter and customers found it actually much more efficient—not surprising when the patent finally explained that a small but effective quantity of organic nitrobody such as picric acid was dissolved therein.

The salesman of one of the glue companies met a series of complaints regarding goods purporting to be glued up with their product, made by some of their customers, each of whom did not, however, buy enough glue to account for his entire output. Whenever any of the output of this group of customers went wrong in the hands of the final consumer, the fault was laid to this company's glue and the trade name suffered. The fault was mentioned to their retainer. Certain peculiarities of their extraction process were taken advantage of and a simple color test devised for distinguishing their glue when in place. A small bottle of reagent and a pocket magnifier in the hands of each salesman enabled him to disprove the calumny on the spot wherever he met it and quickly made it a dangerous statement to continue making.

In one instance the same company was threatened with damages on account of several large lots of bad goods made with their product. The first claim was about \$4,000. The retainer was asked what he thought the trouble was. Examination at the factory of the record samples covering this period indicated the shipments of glue to have been excellent in quality. Examination of a couple of pieces of the goods complained of, showed bad results and suggested dampness. Stained microscopic sections of standard and specially made joints were compared with sections of the bad work shipped out by the user of the glue. Measurements and appearance proved conclusively that the joint was too wet when made, either green wood or overwatered glue and almost beyond question the latter. On the evidence informally submitted the claim was dropped.

A manufacturer of feather boas complained bitterly of the dye

used on the feathers he purchased. It made sore the satiny necks of the wearers, and their feelings, and the retailer. His retainer showed him that the trouble lay nearer home in the angle to which the feathers were trimmed, sharp instead of square.

The makers of a special grade of treated rubber goods who had just had their patent allowed, were planning infringement suits, and through their counsel retained a technical patent adviser. The great economy and advantage lay in the ability to minutely form the goods before treatment, making allowance for the alteration in size during treatment and avoiding all the difficulty of mechanically working the goods after treatment. The process of treatment alone had been described in detail and claimed, though the use of it to make formed articles had been described as one of the advantages. The retainer referred to the literature and found more or less similar treatments though not adjustable as regards change of size produced. He asked a conference of principals and counsel, pointed out the possible confusion of the issue by expert testimony regarding the treatment process, compared with the great simplicity of the case if the patent had a different underlying theory, suggested the theory of a process of producing formed articles of rubber, describing and claiming the novelty of the series of steps, *i. e.*, first roughly forming them, precisely shaping them with allowance for change of size, then treating with corresponding conditions to produce the desired change of size as well as texture. The special treatment claims would be retained at subsidiary to the general invention. Both principals and counsel seized upon the new theory, decided to abandon and refile, deferred suit to be brought under the new patent, and found suit unnecessary because in the new form of the patent there was no chance for defense.

A manufacturer of highly polished sheets had occasionally found trouble with the sort of bloom that appeared irregularly without apparent reason on the polished surfaces. Suddenly the trouble began to increase and he submitted it to his retainer with samples of the bloom sheets. The samples arrived almost simultaneously with the telegram saying the trouble was serious and still increasing. The samples were at once put into the laboratory for analysis, tests and micro examination, a series of questions framed and dictated over the long distance phone. Some of these questions must have seemed ridiculous at the factory. Among the series of twenty or thirty were, "Has the trouble been most noticed in the past in summer, fall, winter or spring?" and "Does the present trouble seem to vary with your weather?" The answers came back after a little and among them were "Noticed more in winter," "Worse on sunshiny, windy days," with the final emphatic comment that seconds had reached \$600 per day. Meanwhile, the work in the laboratory had developed a series of puzzles. That night, after going carefully over the questions and answers, the retainer sent a night lettergram instructing the factory to carefully ground electrically to water or steam pipes every part of one machine and report results. Next afternoon, while still working on the puzzle in the laboratory, the retainer received the telegram—"Grounding stopped trouble immediately; proceeding with grounding of other machines." Just why static charges caused the trouble is too much of a story.

The legal and business representative of a small company operating a secret and very profitable process in the West, came east to sell out on a basis of \$50,000 cash plus royalty to a larger company manufacturing their chief raw material. The business was opening up much larger than the westerners had the means to handle and they were afraid of a rumored combination of the makers of the raw material that might squeeze them hard. They shrewdly figured to get their little wedge into that combination in the nascent state. The president of the Eastern Company was immensely interested in the product, the sample

correspondence and orders, but was not buying a pig-in-a-poke, and could get no secrets from the westerner. Thinking it over in the evening, he called the company's retainer on the phone and asked him to take a hand, so it was arranged that the president would turn over the westerner to him for lunch the next day. The retainer took him out to lunch and started to get acquainted, found that he was dealing with a lawyer, and thought he saw a way. So he discussed the difficulty of negotiating sales of secrets from some experience and carefully avoided asking awkward questions. Finally the western lawyer began to realize the difficulty of the merchandise he had come to market and asked the retainer if any arrangement could be suggested to overcome the dead lock. "You might look up my personal rating that of my company you probably have—then if you want to make me a director of your company on one share of stock you could take my acknowledgment of all information received by me in confidence as director of your company and have me and anyone to whom I revealed it pretty well secured under recent decisions." Naturally, the lawyer jumped at the suggestion, telephoned to the president, and by four o'clock the details were all agreed upon and an appointment made for the following week in the western city. The president and his retainer went west as arranged, only to find that at the last minute the other western man had waxed nervous over the possibility of having to sue the bigger eastern company to recover, and wouldn't accede to the director's suggestions. All day they discussed possibilities, with no result, and at 5 o'clock the president said there was no use staying over. The westerners, too, were ready to give up the deal. But the retainer had a few questions to ask. The westerners said they could guarantee the manufacturing cost, yes; and the selling price for 6 months, yes; and gross sales for the first 6 months equal to the

full amount of cash payment demanded if they had the goods to sell; and they could together get an indemnity bond in that amount as security for this guarantee. The retainer then took the president outside and pointed out that if their sales force were put on his staff their guaranteed cost, selling price and 6 months' sales would yield a profit equal to half the purchase price—or the bond would forfeit—and that there was practically no chance of the second 6 months not showing as well as the first. The president stayed over and the deal was fixed that way.

I believe the general point has been sufficiently illustrated, i. e., that in retainer work the chemical engineer has open to him a sphere of activity in connection with industrial life for which he is peculiarly fitted by training and experience and which parallels in a fascinating way that of the solver of human problems in commercial and social life. One such chemical engineer exhibited to me what I would regard as a treasure, a comment forwarded by the president (whom he knows very well) from a company that has retained him for years.

"The chemist says he doesn't know as you help him so much, but you ask questions and suggest things that set him thinking, and somehow he gets first-rate results. The engineer says you ask more fool questions than anyone that comes around, and he doesn't know how you figure it out, but he does something you suggested and the trouble stops."

May we all be equally fortunate in effects and leave the chief chemists and engineers to their various conclusions. The men at the factory work far better if they feel that a large share of the success depends on them, as, indeed, it does. They are welcome to think it and to their credit, as long as the employer gets the results.

50 EAST 41ST ST., NEW YORK

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE CATALYTIC PRODUCTION OF PETROL

Some particulars are given in the *Times Engineering Supplement* of a catalytic process for the conversion of petroleum almost entirely into petrol. In this method, which is controlled by Messrs. Planes, Ltd., of Birkenhead, England, the petroleum is placed in a high still having a conical bottom passing through the fire bars. A continuous feed of petroleum and of hydrogen under pressure is passed into the still from the bottom, and contained in the still is the nickel used in Normann's process for hydrogenating oleic acid. Strong agitation is maintained by means of a stirrer in the still. The still is heated to a little above the temperature at which petrol or whatever hydrocarbon is wanted becomes a gas. The vapors of petrol or other light hydrocarbon, as the case may be, are carried up by the hydrogen and the heavier hydrocarbons mechanically carried up are condensed in the upper part of the still and fall down, while the light vapors, with the hydrogen, are passed to the condenser. The hydrogen from the condenser is returned to the still. The petroleum, a saturated compound, is thus split up into a saturated hydrocarbon, say, petrol, and a heavier unsaturated hydrocarbon; the latter, it is claimed, at once takes up hydrogen in the presence of the catalyst, and becomes saturated, when it is again broken up into petrol and an unsaturated hydrocarbon, which is again hydrogenated. The process is continued until the nickel becomes inactive and the petroleum in the still becomes overloaded with tarry matters. The tarry compounds and the nickel are then removed, and the latter is regenerated.

THE MANUFACTURE OF COLD-PROCESS SOAPS IN EGYPT

Nadalini (*Chem. Trade J.*, 52, 596) points out that if the cold process for soap-making has now fallen entirely into disrepute

in Europe and America, in Egypt it is very much in vogue for the production of the cheapest quality of household soaps. This is due to the fact that it is possible to produce a soap of good appearance containing many different and cheap fillers, by means of a very simple plant and little knowledge; the Egyptian production is now very great.

The amount of insoluble matter which these soaps contain varies from 20 to 35 per cent and consists principally of talc, calcium carbonate, clay, flour, and various earths. The employment of cottonseed oil is general; the use of coconut oil or other oils of that class containing glycerides of the lower fatty acids has become rare. The caustic soda used is generally the ordinary 60 per cent, at a strength of from 30 to 38° Bé. An ordinary crutcher, frames, a banjo slabber, a cutting machine, and a very simple wooden hand-stamp are used in the manufacture of these soaps, supposed to be an imitation of the Syrian soaps, so well known to the natives. The materials are mixed at the same time into the crutcher, except that gelatine is usually added at the end of the operation, this requiring one hour's stirring. The soap once framed is slabbed after 3 to 4 days, and then is cut into tablets of about 150 grams. Soaps made in Egypt either by the Syrian or the cold process are never neutral; the neutralizing material used is gelatine, rarely sodium bicarbonate, and the use of ammonium compounds or bibasic phosphate is absolutely unknown.

THE PULP-WOOD CONSUMPTION IN CANADA

According to *Paper*, June 18, 1913, p. 34, the bulletin now being issued by the Forestry Branch on the pulp-wood consumption in Canada for 1912 is a compilation of statistics obtained from the sixty pulp mills now operating in Canada. Of the many facts revealed by these figures, there are at least three points

which should be of special interest to the general public, to the forester, and to the trade, respectively.

In 1912, nearly two million cords of pulp-wood were cut in Canada, 47 per cent of which was manufactured into pulp by Canadian mills, an increase of 3 per cent over 1911. This means that over half the pulp-wood cut in Canada is exported in unmanufactured form, principally to the United States. It is estimated in the bulletin that, had this exported pulp-wood been manufactured into pulp in Canada, the increase in the national dividend from this source would be over six and a half million dollars. Yet all the provinces, with the exception of Nova Scotia, have placed restrictions on the exports of raw material, and the fact that, in spite of these restrictions, the quantity of wood exported in the raw state increased from 1911 to 1912, as well as the falling off in Canadian prices for pulp-wood during this period, seems to indicate overproduction on the local market.

Of perhaps special interest to the forester are the statistics showing 40 per cent increase in the use of balsam fir in the manufacture of wood pulp. We quote from the bulletin: "News print can be satisfactorily made from a mixture containing over 40 per cent balsam fir and 60 per cent spruce, and the prejudice against balsam fir is rapidly disappearing." Balsam fir is especially adapted for pulp, the wood being free from resin and having very long, strong fibers. It is, however, good for little else, and is at present viewed by foresters as a "weed-tree." As it is one of the most common species of Canadian trees, the development of a market for this wood will be viewed with satisfaction for both the forester and the private owner.

Of interest to the trade is the successful introduction of the sulfate process in the manufacture of chemical pulp. In this process sulfate of soda is added as a source of alkali and to make good the mechanical losses—10 per cent approximately—in the process of recovery of the soda. Three large Quebec mills used this process in 1912 with excellent results. Spruce, with a small percentage of balsam fir, was the wood used.

SOME PROBLEMS OF THE RUBBER INDUSTRY

Potts (*J. Soc. Chem. Ind.*, 32, No. 11, 564) indicates four leading groups of problems in the rubber industry: (1) Quality of natural raw rubber; (2) Synthetic rubber; (3) Vulcanization; and (4) Regeneration.

The viscosity of Hevea latex diminishes on dilution with water in such a manner as to suggest that it is an emulsion rather than a suspension. Since, however, rubber is an emulsoid colloid, and therefore always a liquid, this does not enable us to draw any conclusion as to the state of polymerization in the latex. The nature of coagulation is not yet fully elucidated, although it is of absolutely vital importance as regards the quality of the rubber produced. On comparing a sample of Plantation rubber with fine hard Para, the latter is preferred. The Para appears harder and "nervier" on the mixing rollers, and in any case it is usually more consistent in quality. Many explanations of this have been advanced, such as the youth of the trees on the Plantations, the acetic acid process of coagulation as compared with the smoking process, etc.; but at present no chemical explanation can be given. Research is also required to determine the nature of the factors affecting quality of raw rubber, and its velocity of vulcanization.

Potts emphasizes the importance of having a raw rubber which shall vulcanize at a constant speed, and, if possible, of guaranteeing this by careful tests before buying. Rubber from which the resins or proteins have been removed will not vulcanize as readily as ordinary technically pure rubber, and the conclusion has been drawn that synthetic rubber will be bad on the ground of being too pure. The rubber manufacturer will not, however, be in any way embarrassed on that account and will be able to add as much resin as is needed, consistent, of course, with specification work.

With regard to the regeneration of waste vulcanized rubber, to Potts' knowledge, so far it has not proved possible to obtain from waste vulcanized rubber a product like raw rubber and containing no sulfur. The combined sulfur is bound with extraordinary strength. What can be accomplished is to remove the free sulfur, some or all of the mineral fillers, and the fibrous materials, and the reclaimed rubber thus obtained by many processes is a valuable adjunct in cheap mixings.

THE EXPORTATIONS OF CAMPHOR FROM JAPAN, 1910 TO 1912

During the last three years, crude and refined camphor valued at the following amounts was exported from Japan (including Formosa), according to *Die Chemische Industrie*, 36, No. 11, 355:

Destination	1910	1911	1912
Hongkong	\$ 6,500	\$ 15,448	\$ 10,956
British India	226,000	285,500	322,000
Straits Settlements	2,450	4,034	4,900
England	327,700	327,700	362,000
France	434,000	398,000	251,500
Germany	178,000	260,000	244,500
United States	393,000	358,000	228,500
Canada	6,000	6,000	10,400
Australia	32,000	47,000	37,850
Other Countries	26,000	24,000	57,800
Total	\$1,631,650	\$1,725,672	\$1,530,406

"SILIT" AND ITS APPLICATIONS IN THE CHEMICAL INDUSTRIES

"Sililit II" is regarded by H. Grossmann (*Chem. Ind.*, 36, No. 10, 304) as a most interesting product. It consists essentially of silicon carbide, and is obtained, according to German Patent 257,468, of July 21, 1911, in the following manner: Silicon, carbon and a binding material, such as colophonium or paraffin, are made up into a plastic mass, shaped in molds of silicon carbide, and finally heated in an atmosphere of carbon monoxide or carbon dioxide to from 1,400° to 1,500° C. At this high temperature the silicon combines with carbon monoxide: $\text{Si} + \text{CO} + \text{C} = \text{SiCO} + \text{C}$. That SiCO is formed has been actually demonstrated by Schützenberger and Colson. If the mass is heated to from 1,600 to 1,700° C., or is heated in an electric furnace, the free carbon combines with the oxygen of the SiCO and escapes as carbon monoxide; there remains silicon carbide. It is obvious that an excess of carbon is always necessary, for without this excess the reduction of the oxycarbide to carbide becomes possible only at a temperature of 2,800° C., and at this temperature a considerable amount of the silicon is lost through volatilization and the molds fuse.

Owing to its great stability at high temperatures, even as high as 1,400° C., and other properties which permit of its mechanical working, "Sililit" may be employed successfully for heating purposes. Like silundum, "Sililit" may be used for electrically heated radiators and hot-plates; a high heat may be obtained from these radiators and hot-plates, without any attending unpleasant odors or accidents. "Sililit" tubes have been successfully employed in the illuminating industry as rods in arc lamps; they have also been used as combustion tubes, and as furnaces for tempering steel pens and other instruments.

Under ordinary atmospheric conditions, "Sililit" furnaces resist a temperature of 1,200° C. for a long period of time. If the furnace is surrounded with a jacket of carborundum, it will resist a temperature of 1,250 to 1,300° C. and a current of 45 volts and 7 amperes for 75 hours, and a heat of 1,400° to 1,450° C. for 5 hours.

"Sililit II" and "Sililit III" are resistant to the action of chemical reagents, particularly acids and chlorine. "Sililit II" cannot be employed as an electrode in the electrolysis of alkali chlorides because of the action upon the carbide of the nascent

oxygen liberated, it may, however, be used in the electrolysis of hydrochloric acid.

"Silit III" consists of silicon carbide and silicon carbonitride. According to German Patent 176,001, of January 4, 1905, it is obtained as follows: Silicon and carbon compounds, or silicon, silicon carbide and an agglutinant containing carbon, are thoroughly mixed and then heated in an atmosphere of nitrogen. The product possesses extraordinary density, hardness and resistance to fluctuating temperatures. It can replace carborundum in the manufacture of whetstones.

THE SCHOOP METALLIZING PROCESS

Sometime ago the Schoop metallizer was described in this column (see *THIS JOURNAL*, 4, 853). At that time no practical results were available; these are, however, brought out in a paper by Albert Neuburger, read before the Märkischer Bezirksverein (*Z. angew. Chem.*, 26, No. 44, 384).

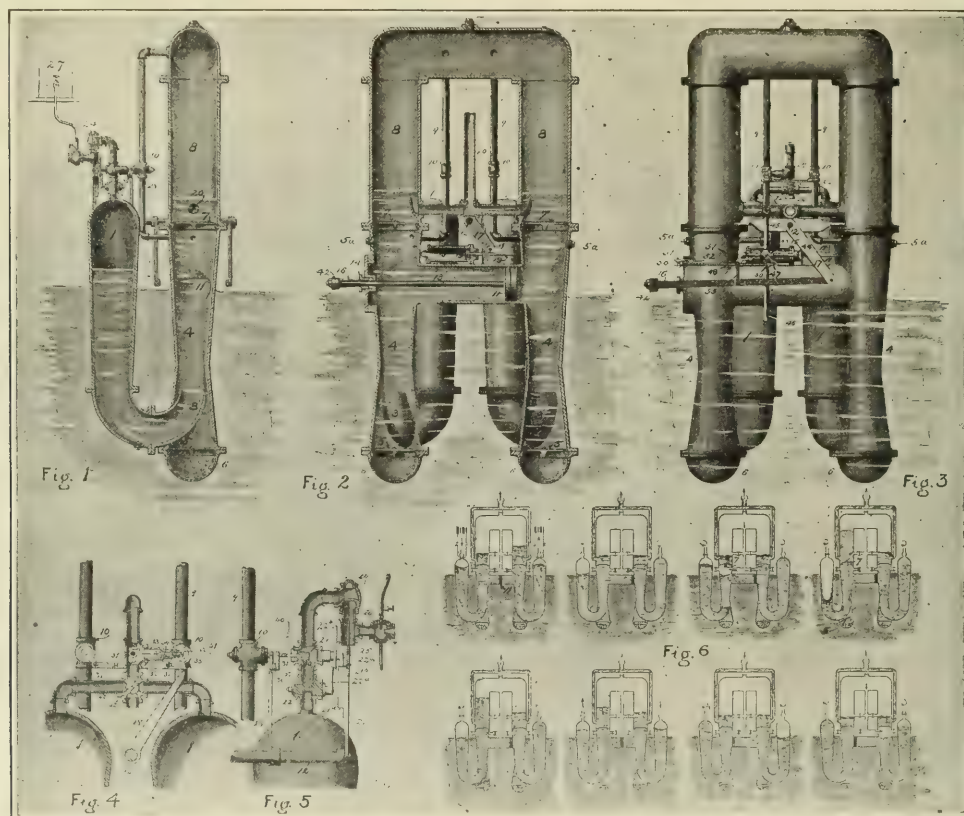
By the old process of galvanizing, not every metal can be made to adhere to another metal without the previous application of a binding metal. In case non-metallic objects are to be coated with metal by this process, they must first be coated with graphite

when a suitable metal is used, rendered uncorrodible. This metallizer draws the metal into wire, fuses it, and, by the aid of an air turbine, converts it into a dust like state; the metal mist is then projected with great velocity upon the object to be coated. Neuburger reports that the fine metal particles adhere to the body and form a solid layer. He considers that Schoop's advice may be used with all metals and for coating all kinds of objects. He has found that the projected metal is very hard; for example, the density of tin deposited by the Schoop metallizer is 14.2 as compared with the density of 9.5 in the case of ordinary fused tin. It is stated that the device may be employed in the construction of accumulators, in the chemical industry (in metallizing glass, quartz glass or iron vessels, etc.), in the canning industry, in the textile industry (for metallizing fibers), etc.

RECENT ACTIVITY IN THE EXPLOSIVE PUMP ART

A review of the more recent internal combustion pumps appears in *Scientific American*, 108, No. 22, 496, from which the following is taken.

The Smyth pump, as shown in the accompanying engravings,



FIGS. 1 TO 5. DETAIL OF THE SMYTH INTERNAL COMBUSTION PUMP FOR RAISING WATER.
FIG. 6. THE CYCLE OF OPERATION OF THE PUMP.

and then placed in baths in which the necessary operations of plating are performed. Structures such as iron bridges, railway stations, etc., are rendered resistant to corrosion by galvanizing or sherardizing, but they remain open to corrosion at the rivet holes. According to Neuburger, by means of the Schoop metallizer even the rivets and rivet holes are metallized, and,

is a duplex one, both parts being alike. A combustion chamber, 1, the lower end of which is merged into a nozzle, 3, extends into a casing, 4, which constitutes the suction pipe of the pump. The lower end of this casing is provided with a check valve, 5, and a strainer, 6, and the upper end is separated from an air chamber, 8, by the check valve 7. As seen in Figs. 1 and 2, the discharge

of the pump is through a pipe, 20, which connects with each air chamber, 8. Two pipes, 9, having valves, 10, to control the flow of air or water, connect the air chamber, 8 with the casings 4 just below the valves 7. A water piston, operated by the explosive charge, is located in each chamber, 1, and the two casings 4. Air is introduced into the air chamber by means of valves 5a.

To regulate the position of the water piston in the chamber 1, an independent piston, 11, free to move in response to heat pressure, is provided in the pipe connecting the two casings 4. This piston is actuated by the power piston 19, in the motor cylinder 15, through the link 18, lever 17 and rock shaft 12 and link 16 connected by the yoke 42 to the rod 13, which passes through a stuffing box, 14.

As seen in Fig. 3, the motive fluid for operating the motor 15 is introduced and exhausted to and from the cylinder by a four-way valve, 43, through pipes 45, 44 and 46. This valve is operated by the link 16, carrying the tappet 53, which actuates the levers by riding over the cam surfaces 52. These levers 51 operate in turn, by means of the spring-operated tappets 50, the sliding tappet lever, 48, which oscillates the lever 47 of the valve 43.

The apparatus for introducing an explosive mixture is shown in detail in Figs. 4 and 5.

A fuel reservoir, 27 (see Fig. 1), is connected to a vaporizer, 26, which communicates with the combustion chambers 1 by a pipe controlled by the poppet-valve 24 and pipes 23 leading to a four-way valve, 22. The sparking device, located in the chamber 29, consists of a rocking wiper, 30, secured on the shaft 31, which is provided with an operating lever, 32, and a flat spring, 33, attached to an insulated rod, 34. The wires 40 and 41 connect the sparking device with a battery not shown. The tappet arm 28 on the shaft 12 operates both the valves 10 and the wiper 30 by means of the slotted link 36 carrying the pins 37 and 38.

The valve 22, which controls the flow of gases to or from the combustion chambers, is also operated from the rock shaft 12 by the tappet 21, the latter having a cam surface, 21a, which operates one arm of a loosely pivoted bell crank tappet lever, 22c. This arm of the tappet lever 22c engages with the slotted link 22b, which is loosely connected to the handle 22a on the stem of the valve 22. The other arm of the lever 22c constitutes a tappet which, by engaging the part 21b of the tappet 21, operates the spring-actuated valve stem 25 of the check valve 24, so that the tappet 21 serves the double function of reversing the valve 22 and keeping the valve 24 open. The operation is now evident.

Motion is imparted to the piston 11 by the motor 15, which causes the water piston to move in the chamber 1 and make room for the charge in this chamber. The valve 22 being properly disposed, the action of the piston 11 and the travel of the water piston cause successive inflow of explosive charges and scavenging of the spent gases.

If the explosive charge is assumed to be in chamber 1, the water piston will extend nearly to the valve 7, separated from the water and pressure in the air chamber 8 by this valve and by whatever air has been permitted access through the valve 5a. At this point the valve 10 is opened by engagement of the tappet arm 28 with the link 36 and the compressed air, or water under pressure from the air chamber, consequently flows beneath the valve 7. Thus the water piston is forced back against the charge, compressing it to the pressure of the air chamber, which is, of course, that of the head. The charge is prevented from escaping by the closing of valve 24.

Ignition now takes place, resulting from the engagement of the tappet pin 37 with the end of the slot in the link 36, thus rocking the wiper 30 past the spring 33 by the connection of the link 36 to the wiper arm 32. The slot in the link 36 permits the valve 10 to close the moment the wiper arm 32 passes out of

engagement with the spring 33. The expansion of the gases in the chamber 1 causes the water piston to be driven with great energy and speed through nozzle 3.

The spaces vacated in the chamber 1 and casing 4 are filled instantly (practically simultaneously with the expansion) by air through valve 5a. That portion of the air admixed with the spent gases in the casing 4 of the expansion chamber will be cut off and separated from that in the charged chamber 1 by the incoming water through valve 5. The portion of air and gas in the casing 4 is thus trapped beneath valve 7, ready to be driven into the air chamber at the next operation of the water piston. That portion of the spent gases and air in the chamber 1 will pass out as exhaust. The cycle of operation of the Smyth pump is shown in Fig. 6, and described as follows:

1. Explosive charge being taken in the left-hand chamber and discharging the spent gases from the other chamber, the piston 11 being midway of its stroke, traveling to the right.

2. A fresh charge in the left-hand chamber and the right-hand chamber completely occupied by the water piston, the spent gases of the previous explosion having been driven out by the water.

3. Charge in the left-hand chamber compressed to less than half of its original bulk by the admission of air pressure between the water piston and the check valve 7.

4. Expansion of charge due to explosion and the travel of the water into the air chamber, preceded by the volume of air from beneath the valve 7. The inrush of the water through the lower check valve 5 induced by the injector, gravity and atmospheric pressure is also shown.

5. Left-hand chamber almost filled with water.

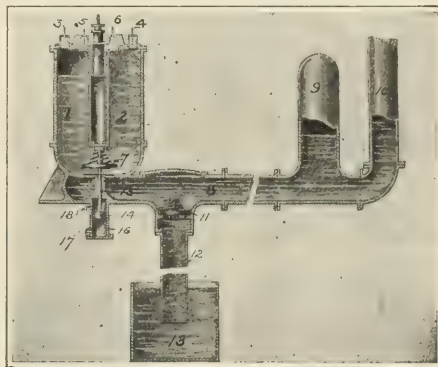


FIG. 7.—THE CHANCE APPARATUS FOR OPERATING INTERNAL COMBUSTION PUMPS AND COMPRESSORS

6. Condition similar to 1, but reversed as to direction of the flow of gases and the movement of the water piston.

7. Charge in the right-hand chamber. The left-hand chamber is completely scavenged of spent gases from previous explosion.

8. Explosive charge in the right-hand chamber ready to be ignited, thus completing the cycle.

It has been the custom in explosive pumps having two combustion chambers to cause the charge to be drawn into one chamber by the continued travel of the liquid piston after the waste gases in the other chamber have dropped to low pressure. In pumps of this character the continued travel of the liquid piston must be sufficient to draw in the new charge; the expulsion of the waste gases is accomplished by the return stroke of the piston and must be completed before the return stroke can compress the charge in the other chamber.

The necessity for prolonging both the out stroke and the return stroke of the piston to permit the drawing in of the charge and the expulsion of the waste gases, introduces elements of

time by which the capacity and speed of operation of the pump are correspondingly reduced.

H. M. Chance and T. M. Chance, of Philadelphia, Pa., have devised a method of operating such pumps whereby the rapidity of action is increased by decreasing the time necessary for each stroke and return stroke.

The apparatus, as seen in Fig. 7, comprises two combustion chambers 1 and 2 provided with inlet valves 3 and 4 for the introduction of the combustible mixture and two exhaust valves 5 and 6 for the discharge of the waste gases.

A spring-pressed valve, 7, which controls the communication between the two chambers 1 and 2, is operated by the rod 15 and piston 14 in the cylinder 16. This cylinder communicates with the liquid in the chambers 1 and 2 by the passage 17, and the connection 18 leads to a source of pressure slightly greater than that at which it is desired to exhaust the waste products of combustion. The usual conduit 8 is connected to the air chamber 9, delivery pipe 10 and suction pipe 12 with inlet valve 11. This suction pipe 12 is connected with the source of supply 13.

Let it be assumed that the chamber 1 contains a compressed combustible charge which has just been ignited, the valve 7 being open, the liquid in the conduit 8 is given a high velocity,

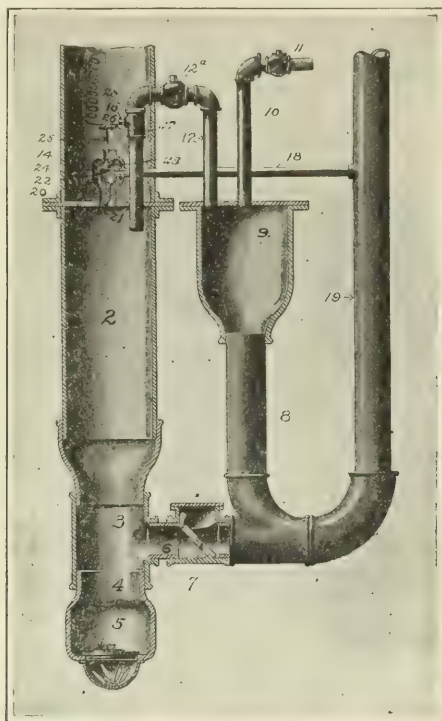


FIG. 8 THE WHITE PUMP FOR UTILIZING FULL STATIC PRESSURE IN COMPRESSING THE CHARGE

When the pressure in the chamber 1 falls below the predetermined pressure at which it is desired to open the exhaust, the valve 5 is opened and the valve 7 closed by the piston 14, operated by a pressure slightly greater than that now existing in the chamber 1, the scavenging taking place at atmospheric pressure. The liquid in the chamber 2 now falls by gravity; the inlet valve 4 opens; and a new combustible mixture enters the chamber 2. At the same time the liquid rises in the chamber 1, expelling the waste gases. The valve 4 then closes.

Upon commencing the return stroke the liquid in the conduit 8 opens the valve 7, forcing the liquid into the chamber 1 and

closing the valve 5 by the impact of the liquid. The momentum of the liquid in the conduit 8 now causes the liquid to rise in the chamber 2, compressing the charge in that chamber. The cycle is then repeated.

It will thus be seen that a new charge of combustible mixture is introduced while the products of combustion are being discharged, obviating the necessity for prolonging both out stroke and return stroke, and in this manner increasing both the speed and the capacity of the pump.

In explosive pumps it has been the custom to compress the combustible charge in the same chamber in which it is exploded. A recent invention of C. E. White, of San Francisco, Cal., is a pump in which the charge is first drawn into a separate chamber and forced thence into the usual combustion chamber by the pressure of the liquid in the delivery pipe. By this means, it is claimed, the full static pressure is utilized in compressing the charge.

The White pump, as shown in Fig. 8, comprises a combustion chamber, 2, connected to the supply pipe 4 having the usual inlet valve 5, by the tee 3, which communicates with the delivery pipe 19 through the pipe 6, in which is placed a check valve, 7. This delivery pipe 19 is connected to the gas chamber 9 by a pipe, 8.

The gas supply pipe 10, having the check valve 11, communicates with the chamber 9, the latter being connected with the chamber 2 by the pipe 12 having a check valve 12a.

The exhaust valve 14 comprises a cup, 20, provided with a bored extension, 21, and a diaphragm, 22. This diaphragm 22 is provided with a valve, 23, adapted to enter a seat, 24, the stem 25 of the valve 23 is provided with a contact, 26, to bridge the terminals 27 and 28 to close the circuit of the spark plug 16. A pipe, 18, connects the delivery pipe 19 with the cup 20.

Let it be assumed that the pump is filled with liquid and an explosive mixture, the contact 26 closes the ignition circuit through the terminals 27 and 28 and the charge is exploded. The liquid is thus forced through the pipe 6, closing the valve 5 and opening the valve 7. The liquid in the chamber 9 and pipe 9, moves downwardly, creating a suction in the chamber 9, whereupon the valve 11 opens and causes a fresh supply of gas to be drawn into the chamber 9. As the liquid moves upwardly in the pipe 19, the pressure on the diaphragm 22 is removed, and the contact 26 is moved downwardly, permitting the escape of the waste gases.

After the explosive force is spent, the liquid in the pipe 19 closes the valve 7 and the liquid piston in the pipe 8 and the chamber 9 forces the explosive mixture into the chamber 2 and compresses the charge against the water, which has by this time risen in the chamber 2.

The cycle is then repeated.

In internal combustion pumps it has been necessary after each explosion to draw in a fresh charge of gaseous mixture from an outside source. This has necessitated gas and air connections which are impracticable when such pumps are used in mines and in many other instances.

To obviate this difficulty, Poore and Harvey, of London, England, have recently constructed a device which generates its own gas by the electrolysis of water. No pipe connections whatever except those used for suction and delivery of the water are thus needed.

In Fig. 9, the current for decomposing the water is supplied by the dynamo *L* to the contact *L*¹, which makes a sliding contact with the chamber *G* at prearranged periods of time. The upper part *B* of the body *A* of the pump forms the explosion chamber. The gases formed by the electrolysis of the water are mingled with air introduced in the chamber *B* through the air valve *M*, and are exploded by the spark plug *K*¹.

The ignition circuit comprises a primary winding, *J*, having a battery, *J*¹, and switch, *J*², and a secondary winding, *K*. The

float *F*, carried by the lever *H*, which is pivoted at *H*¹, operates to close the firing circuit.

The apparatus is operated by closing the switch *J*² and turning on the decomposing current. The float *F* is then in its lowest position, and the contacts *L*¹ are in contact with the chamber *G*.

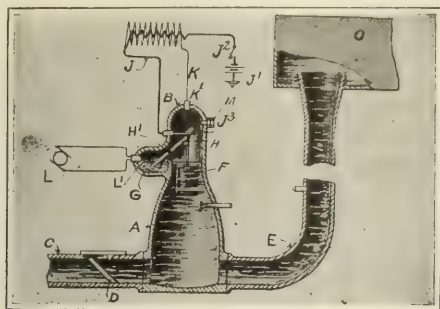


FIG. 9 POORE AND HARVEY DEVICE FOR GENERATING ITS OWN GAS BY THE ELECTROLYSIS OF WATER

As the water rises, the float *F* moves the chamber *G* out of contact with the contact *L*¹ and, rising still farther, causes the lever *H* to contact with the contact *J*², thereby closing the primary circuit. The charge is then fired by the plug *K*¹.

The force of the explosion expels the water up the delivery pipe *E* into the tank *O*, and also draws a fresh supply of water through the suction pipe *C*. The return movement of the water closes the check valve *D* and compresses the new charge of explosive mixture. The cycle is then repeated.

The pipe *N* is used to form a spray for condensing the vapor caused by the explosion.

THE ALKALI INSPECTOR'S REPORT FOR 1912

The forty-ninth annual report of the Chief Inspector of Alkali, etc., Works for England, Ireland and Wales, which was issued during July, is reviewed in *The Chemical Trade Journal*, 53, 49.

The number of works registered under the Act during 1912 was 1,305, of which 73 were "alkali works." The general average amounts of acid escaping from the exits for waste gases in works under inspection showed slight variations from the preceding year. The acidity of gases of all chimneys, however, showed a distinct increase, being equivalent to 1.218 grains of sulfuric anhydride per cubic foot, as compared with 1.192 grains during 1911. This increase was mainly due to those works wherein ores containing metallic sulfides were calcined.

For many years past there has been a slow but continued reduction in the number of works registered as sulfuric acid works. This has been due to the increase in aggregate production accompanied by the closing of works of small capacity, concurrently with increased productive capacity in other works already in operation. The various forms of mechanical burner came into more extended operation during 1912. The use of fans also—so efficient in maintaining constant working conditions—became more widely adopted. There is a general tendency to appreciate the advantages of increased Gay-Lussac tower space, and in many works this has been increased. The "Opl" system continued in constant use, and during 1912 a second installation of this system was put into successful operation. So far as regards the escape of noxious gases, both of these sulfuric acid plants gave every satisfaction; but it is still too soon to express an opinion as to wear and tear. Mention is made of a fatality which occurred in a sulfuric acid works during the removal of packing from a Gay-Lussac tower, owing to the presence of oxides of nitrogen.

Those sulfuric acid works in which the catalytic or contact processes were used were conducted during the year without any marked change in methods of working, nor was there any change in the number of works, although extension of plant effected an increase in the capacity for production. The methods previously in operation for the concentration of sulfuric acid continued in use. Undue escapes of acid gases were observed coming from over-heat pans on several occasions; these irregularities were associated with the methods of firing and with the disposition of the fireplaces. The Kessler system continued to yield exit gases low in total acidity and to operate in a regular way. The use of fans instead of the original steam-jet form of draught-inducer was further extended. The cascade system gained in favor and is now in widely extended operation; silica ware and tantiron continued to be used as materials of construction of the evaporating vessels. The Gaillard tower continued in use, generally with satisfactory results as to escaping gases, but in one works there was much trouble.

The chemical manure works were kept actively in operation during 1912. 14,115 tons of guano, 520,270 tons of mineral phosphates, and 123,580 tons of nitrate of soda were imported during the year. The exports of ammonium sulfate amounted to 287,000 tons, as compared with a home consumption of 90,000 tons. The use of mechanical methods for dealing with products was extended during the year, and the direct method of producing ammonium sulfate was put into more extended employment, chiefly the coke-oven works. The loss of ammonia during the handling and storing of ammoniacal liquor is very considerable. Attention continued to be given during 1912 to the formation of ammonium sulfate from gases containing ammonia and hydrogen sulfide, without the use of sulfuric acid, but so far as practical production in England is concerned it cannot be said that permanent success has yet been obtained.

The bulk of the chlorine was produced in alkali works, and, as these works were seriously affected from the temporary scarcity of fuel, the production of chlorine was restricted for a time. The mechanical arrangements for the production of bleaching powder continued to work satisfactorily, and their use was further extended.

A further increase in the number of tinplate flux works was noted, the total registered being 73. Great activity was apparent in the earlier part of 1912, but towards the end of the year the demand for tinplates was decidedly lessened. The methods in use in the recent past for minimizing the escape of hydrochloric acid from these works proved satisfactory in all cases in which efficient means were provided for washing the furnace gases or for washing the scruff before this was charged into the furnace for roasting. The general average escape of hydrochloric acid fell from 0.219 in 1911 to 0.170 in 1912.

The number of sulfide works under inspection increased from 69 in 1911 to 78 in 1912. During the year four works in which certain sulfide colors were manufactured came under consideration and were found to require registration in this class. Much improvement inside these works as well as to their immediate neighborhood has been effected as the result of inspection, and what was formerly an objectionable escape of a noxious gas has been entirely removed. This desirable result has been attained partly by the provision of means for preventing access to the air of any hydrogen sulfide evolved, and partly by reducing the amount of noxious gases requiring to be dealt with through improvements in methods of manufacture.

The total number of lead poisoning cases reported from all industries in 1912 was 587, of which number 44 were fatal, as against 669 (37 fatal) in 1911. Only 5 cases of arsenic poisoning occurred, and 3 of these were due to the handling of bird skins imported from the West Indies; a fourth case occurred to a workman employed in a paper mill in dissolving block tin in concentrated hydrochloric acid. Although helmets and air

tubes, or similar apparatus, with compressed oxygen or air, are supplied in many works, folds of flannel still seem to be the more general form of respirator.

WANTED: NEW USES FOR BROMINE

A prize of \$2,500 is offered by the Deutsche Bromkonvention G. m. b. H., Leopoldshall-Stassfurt, Germany, to the discoverer of a process or compound leading to a new or an increased consumption of bromine. The following are some of the conditions attached to this competition: The new discovery must represent a technical innovation and must not adversely affect existing uses of bromine. The process must be applied in practice at the latest one year after the awarding of the prize. The process must, in the opinion of the jury, lead to a considerable increase in the European consumption of bromine at a suitable price. Competitors must send in their processes by January 1, 1914, at the latest.

THE RADIUM MARKET

There has recently been a marked reduction in the prices of radium preparations. Earlier in the year radium bromide sold for \$105.60 per milligram in Germany; and, in April, a New York firm offered for sale any part of 800 milligrams of radium bromide, gauging from 25 per cent to 90 per cent purity, to be delivered in tubes of 10 to 125 milligrams capacity, at \$90 to \$100 per milligram. In July, however, the K. K. Montan-Gesellschaft in Wien, which produces radium salts from pitchblende, made sales at \$43.20 to \$52.80 per milligram, depending upon the activity. The recent decrease in price is thus explained in *Chemie*, 6, No. 1530: During the last three years, mesothorium, as well as radiothorium, began to be employed in place of radium, especially in medicine. Mesothorium is obtainable at a cost of \$32.40 per milligram in Germany and, in addition, may be procured four times more active than radium. While the life of mesothorium is short, by mixing it with radium salts a preparation of long life may be obtained. The total production of radium bromide per year is between 2 and 3 grams. In 1911, the radium preparations produced by the Austrian Radium-praeparatefabrik amounted to 14.146 grams, containing 2.647 grams of pure radium chloride, valued at \$214,900.

The Radium Hill Company conducted operations in 1912 in Australia which resulted in the production of 2.5 milligrams of pure radium bromide; it is reported that 350 milligrams more are in the laboratory in various stages of purification. Recently two American firms have been organized for the preparation of radium salts, etc.; these are the Radium Company of America, of Philadelphia and Sellersville, Pa., and the Radium Chemical Company, of Pittsburgh, Pa. The latter company is marketing radium salts and applicators, radium drinking water, radium bath water, radium compresses, and radioactive earth.

THE MANUFACTURE OF COPPER WIRE BY ELECTRO-DEPOSITION

According to the *Brass World*, W. E. Gibbs has devised a process for the manufacture of copper wire by electrode position. Previous attempts to accomplish this object have been unsuccessful.

The Gibbs method requires a fine copper wire as a core for making the desired product, and the additional copper is deposited on it while it moves through a tank containing the solution. The fine copper wire is made endless and passed through a regular plating solution containing sulfate of copper and a little sulfuric acid. The wire passes over grooved rollers operated from outside while passing through the tank. After leaving the tank, the wire passes through a small rinsing tank to remove the solution, and then goes to a reel around which it passes a number of times, returning again to the plating tank. The

plating may thus be continued until the required thickness is obtained.

THE MELTING POINTS OF ELEMENTS OF ATOMIC WEIGHT 48 TO 59

Burgess and Waltenberg¹ have determined the melting points of the refractory elements of the iron group by means of the micropyrometer,² obtaining the following results:

Metal	Melting point with micro-pyrometer	Purity Per cent.	Probable melting point of pure element
Nickel.....	{ 1452°(a) 1449(b)	99.83s	1452° ± 3
Cobalt.....	{ 1477 ± 2 1478 ± 1(c)	99.95s	1478° ± 5
Iron.....	{ 1533 ± 1(d) 1528(b)	99.98 ± 01	1530° ± 5
Manganese.....	1255	97 to 98	1260° ± 20
Chromium.....	1520	98 to 99	1520° to > Fe
Vanadium.....	1720	97 to 98	1720° ± 20
Titanium.....	1794 ± 12	99.9+	1795° ± 15

(a) Assumed value on platinum strip; also observed value on iridium strip.

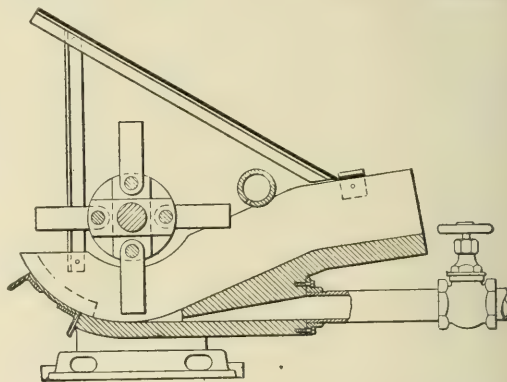
(b) Crucible melts in electric furnace.

(c) Crucible melts in electric furnace; also on iridium strip with micro-pyrometer.

(d) Five samples all agreeing to within 3°.

THE GRANULATION OF SLAG

Recently G. Juntzen described a method of granulating slag by means of a jet of air before the German Metallurgical Association. In this procedure, which has been in use for over a year at the Buderus Works, where about 100 tons are produced daily, the slag run from the furnace is conducted through a conduit to a rotating drum 45 feet in length and 6 feet in diameter. Upon entering this drum, it is met by a jet of compressed air, which throws it against the sides, which are kept cooled by the exterior circulation of water; in this way the disseminated



DEVICE FOR GRANULATING MOLTEN SLAG

slag always encounters cool surfaces. Scrapers within the drum prevent adhesion of the slag, which eventually is removed at the bottom end of the cylinder in small grains, said to be without lumps. It is claimed that the slag thus reduced is more satisfactory for cement-making than that granulated by water; it is dry and also more dense. Such granulated slag is suitable for use as sand.

In the process of J. T. Bergwith for the granulation of blast-furnace slag, the attempt is made to produce a dry granulated slag, notwithstanding the employment of water.³

¹ *J. Wash. Acad. Sci.*, 3, No. 13, 371.

² *Bull. Bureau of Standards*, 9, 475.

³ *Eng. Min. J.*, 96, 55.

This is done by delivering the stream of molten slag to the action of a rotary feeder, driven at a high rate of speed, the feeder members of which scrape or shear off extended portions of the stream of slag and project it upward into the air. Simultaneously with the separation of the portions of slag from the main stream by the feeders, it is subjected to the action of a small stream of water, which combines with the feeders to produce the granulating action. During its flight through the air, it cools and dries, so that it is deposited in a nearly dry granulated state. As may be seen from the accompanying illustration, the lower portion of the feeder wheel runs in a suitable trough or runner, the sides of which rise nearly to the hub of the wheel. A guard bar, or shield, is arranged above the wheel. The trough, or runner, is approximately V-shaped in cross-section before it reaches the disintegrator, but broadens out to a flat-bottom trough in that portion which underlies the feeder blade. At a point approximately central to the lowermost part of the trough, a wide, relatively thin water inlet communicates with the trough. The feeder wheel comprises a number of plates supporting rods, or bars, separated by a number of face blocks.

SOME INNOVATIONS IN THE PAPER INDUSTRY

Philip B. Sadtler, of the Swenson Evaporator Company, of Chicago, Ill., has pointed out that by employing a battery of blow tanks to systematically wash the liquor out of the pulp, this may be accomplished with the least expenditure of water and the highest cleansing effect. This is, moreover, said to be one of the best methods for eliminating the objectionable odor of the sulfate pulp mill. Pulp is blown under pressure from the digesters directly into the blow tanks, the battery being used in countercurrent system for washing. The small expenditure of water leaves a minimum of water to be evaporated.

An idea which Mr. Sadtler has included in the design of the apparatus in the Chesapeake Pulp & Paper Company, at West Point, Va., is the use of waste heat gases from the rotary black ash furnaces to produce the generation of steam in the boiler; this steam is then used to carry out the evaporation of the black liquor in the evaporator. This idea of employing waste heat from special furnaces to generate steam in boilers is a novelty, it is said, in the pulp field.

THE GAS AND ELECTRIC CONSUMPTION IN GREATER NEW YORK

The Coal and Coke Operator, 21, No. 11, 231, reports that there were 1,101,174 consumers of gas in Greater New York in 1912. The 13 different gas companies which make and sell this product made and bought during the year 55,542,488 cubic feet of gas, of which 47,775,188 cubic feet were sold to consumers. The Consolidated Gas Company had a total of 483,727 consumers, while the Brooklyn Union Gas Company had 361,845.

The electric companies generated and bought 702,174,871 kilowatt hours of electricity and sold 518,294,646 kilowatt hours. The reports of the six electric companies serving Greater New York show that there were 229,758 active meters in operation; of these, the New York Edison Company had 168,814 active meters and the Edison Illuminating Company of Brooklyn 41,684.

THE CONSUMPTION OF THORIUM IN THE UNITED STATES

It is noted in the *Chemiker-Zeitung*, 37, No. 77, 776, that the only company in the United States which produces thorium compounds from monazite sand is the Welsbach Company, of Gloucester City, N. J., although there are two or three other concerns which obtain thorium from waste Welsbach mantles. The mining of the monazite deposits in the Carolinas, which supplied 1½ million pounds in 1912, has been discontinued, owing to the decrease in the import tax from 6 cents to 4 cents per pound. The number of gas mantle factories has diminished from 89, in 1909, to 50, the most of which are found in the States of Ohio, New York, Pennsylvania, and Illinois. In all, 65 million mantles are manufactured per year, of which 40 per cent are made by the Welsbach Company. The consumption of thorium compounds for this purpose amounts to about 220,000 pounds, more than half of which is imported from Germany. The duty on thorium salts, gas mantles and spent mantles is 40 per cent of their value. According to a report made by the General Gas Mantle Company, of Camden, N. J., the cost of 1,000 incandescent gas mantles is \$42.07 in New York, and the German manufacturers can sell the same for \$42.50, including the import tax.

SCIENTIFIC SOCIETIES

SOCIETY FOR PROMOTION OF ENGINEERING EDUCATION

The twenty-first annual meeting of the Society for the Promotion of Engineering Education was held at the University of Minnesota, Minneapolis, June 24 to 26. Among the conspicuous features of the program as reported by *Engineering Record*, July 12, 1913, were a series of papers on the design and construction of buildings for technical schools, papers on hydraulic engineering education presented at a joint session with the American Water Works Association, a symposium on highway engineering education, a paper by a representative of the Pennsylvania Railroad on coöperation between technical schools and the industries, and a paper by a prominent manufacturer advocating a movement in the direction of standardization of technical terms.

Last year at the Boston meeting of the society a number of experts on scientific management showed that there was a connection between this subject and education. This year Director H. S. Person, of the Tuck School of Administration and Finance, Dartmouth College, was requested to apply the principles of scientific management to college administration. In doing so he showed that by functionalizing college work greater efficiency can be obtained than by present methods. The functions involved in education are teaching, administration, advising, and guiding non-classroom educative influences. As teachers

are not equally fitted for all functions, it is advisable to assign to each only those for which he is best adapted.

At a session held jointly with the American Waterworks Association, Prof. D. W. Mead, of the University of Wisconsin, and O. L. Waller, of the State College of Washington, read papers covering the preparation of young men as hydraulic engineers. The authors showed that the best preparation for a hydraulic engineer is that which will teach him to think. As Professor Mead stated, the value of any education is not so much in the acquirement of knowledge as in the ability to acquire it. He pointed out that the tendency of educational methods is to discourage the development of judgment, for the students are apt to accept the dictum of their teacher as infallible and hence not subject to their critical inspection.

Professors Sherman and Schlaflay, of the Ohio State University, explained how their students are encouraged to get into commercial work in the summer time. If this is impracticable, the instructors take commercial contracts and employ the students as assistants. These "practical" summer surveying camps take the places of "practice" camps and are giving excellent results. Under this plan the students feel and act more like engineers than under the old plan. Prof. F. P. McKibben, of Lehigh University, gave details of the experience of his students

in obtaining summer employment and of the excellent results obtained therefrom. The discussion brought out a general sentiment in favor of the use of the summer months in actual work and emphasized the duty of future employers of the men to provide such work for them.

A marked tendency to lengthen the college course to five or even six years has been conspicuous of late. A number of schools have introduced longer courses, these being either required or optional. This tendency is opposed by some leading educators, and two of them, President A. C. Humphreys, of the Stevens Institute of Technology, and Prof. G. F. Swain, of Harvard University, vigorously voiced their opposition at the Minneapolis meeting. They claim that four years cover a period long enough for a boy to remain from actual work and that the expenditure of an extra year or two does not bring commensurate results. In championing the other side the advocates of the longer course pointed out that the extra time is not wanted for more technology but for studies selected to prepare for better citizenship, and that on this basis its use is justified. Obviously no agreement was reached or could be reached as to the proper length of a course, but the discussion served to keep the topic alive and to put the authorities in charge of technical schools in a defensive attitude toward their present practice, whatever that may be.

A subject which affects all engineers, because it relates to the ease and understanding with which they can read technical literature, is the standardization of technical terms. Mr. D. M. Wright outlined the results of his experience in a paper in which he recommended the appointment of a committee to study the subject.

At the request of the society a representative of the Pennsylvania Railroad, Mr. Ivy L. Lee, gave the results of the experience of that company with the many technical graduates who have entered the company's employ. The faults which they have noted are a lack of practical experience and judgment, an idea that they are far superior to the rest of mankind, and a certain narrowness of mind, inculcated through a too exclusive attention in college to mathematics and theoretical science and to a too great neglect of those broader subjects such as political economy, history and general literature.

Mr. Lee believes that these faults can be overcome and that by directing attention to the shortcomings and limitations as well as the strong points of the students, teachers can do much to assist them in eliminating their weaknesses.

Of all the difficult concepts which students have to grasp that of the relation of force, mass, weight and acceleration is one requiring possibly the greatest mental effort. Teachers of mathematics, physics, mechanics and engineering struggle with it. The situation is aggravated by the use of many different units for these quantities. Prof. E. V. Huntington, of Harvard University, proposed a simplification of these by eliminating most of these units and substituting what he calls the "standard" weight and the "local" weight for the usual "mass" and "weight." Naturally a proposition like this stirred up much discussion and the whole subject was referred to a special committee on the teaching of mechanics to engineering students, which was appointed forthwith, with Prof. E. R. Maurer, of the University of Wisconsin, as chairman.

The cause of the much-discussed thesis, once an essential part of the engineering curriculum, was championed by Prof. H. Wade Hibbard, of the University of Missouri, and many other teachers.

In his presidential address Prof. William T. Magruder, of the Ohio State University, painted a picture of an ideal instructor.

A number of committees appointed last year to study the improvement of instruction in the several branches of engineering reported progress and were continued for another year with instructions to carry out their own suggestions. The chairmen

of these are Profs. F. P. McKibben, of Lehigh University; C. F. Scott, of Yale University; A. M. Greene, Jr., of Rensselaer Polytechnic Institute; and F. W. Sperr, of the Michigan College of Mines. The committee on college administration, which made a report covering such matters as the salaries of professors, falling off in the number of technical students, leaves of absence, etc., was continued. A new committee on the teaching of physics to engineering students, with Prof. G. V. Wendell, of Columbia University, as chairman, was also appointed. Altogether the society has a large amount of committee work in progress, greater than at any other time in its history.

The following elections occurred this year: *President*, G. C. Anthony, Tufts College, Mass.; *Vice-Presidents*, H. S. Jacoby, Ithaca, N. Y. and D. C. Humphreys, Lexington, Va.; *Secretary*, H. H. Norris, Ithaca, N. Y.; *Treasurer*, W. O. Wiley, New York, N. Y.; *Councilors*, H. W. Tyler, Boston Mass.; J. F. Hayford, Evanston, Ill.; A. S. Langsdorf, St. Louis, Mo.; S. M. Woodward, Iowa City, Ia.; M. S. Ketchum, Boulder, Col.; F. P. Spalding, Columbia, Mo.; and P. F. Walker, Lawrence, Kan.

Several important actions were taken at the meeting. The council voted to take the steps necessary to bring before the membership a plan to make the secretaryship permanent. Princeton was recommended for the 1914 meeting and California for the year following. The secretary was instructed to confer with the officers of other societies with a view to reducing the conflict between convention dates.

INTERNATIONAL ENGINEERING CONGRESS, 1915

In connection with the Panama-Pacific International Exposition which will be held in San Francisco in 1915, there will be an International Engineering Congress, in which engineers throughout the world will be invited to participate. The congress is to be conducted under the auspices of the following five National Engineering Societies: American Society of Civil Engineers, American Institute of Mining Engineers, The American Society of Mechanical Engineers, American Institute of Electrical Engineers, and The Society of Naval Architects and Marine Engineers. These societies, acting in cooperation, have appointed a permanent Committee on Management, consisting of the Presidents and Secretaries of each of these Societies, and eighteen members resident in San Francisco.

Thus constituted, the personnel of the Committee is as follows:

FOR THE AMERICAN SOCIETY OF CIVIL ENGINEERS.—Geo. F. Swain, *President*; Chas. Warren Hunt, *Secretary*; Arthur L. Adams, W. A. Cattell, Chas. Derleth, Jr., Chas. D. Marx.

FOR THE AMERICAN INSTITUTE OF MINING ENGINEERS.—Charles F. Rand, *President*; Bradley Stoughton, *Secretary*; H. F. Bain, Edw. H. Benjamin, Newton Cleaveland, Wm. S. Noyes.

FOR THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS.—W. F. M. Goss, *President*; Calvin W. Rice, *Secretary*; W. F. Durand, R. S. Moore, T. W. Ransom, C. R. Weymouth.

FOR THE AMERICAN INSTITUTE OF ELECTRICAL ENGINEERS.—Ralph Davenport Mershon, *President*; F. L. Hutchinson, *Secretary*; J. F. De Remer, A. M. Hunt.

FOR THE SOCIETY OF NAVAL ARCHITECTS AND MARINE ENGINEERS.—Robert M. Thompson, *President*; D. H. Cox, *Secretary*; Geo. W. Dickie, W. G. Dodd, Wm. R. Eckart, H. P. Frear.

The Committee has effected a permanent organization, with Prof. Wm. F. Durand as Chairman, and W. A. Cattell as Secretary-Treasurer, and has established executive offices in the Foxcroft Building, 68 Post Street, San Francisco.

The Presidents and Secretaries of the five national societies will constitute a Committee on participation, through whom all invitations to participate in the Congress will be issued to governments, engineering societies, and individuals.

The actual management of the Congress and the work of securing and publishing papers will be in charge of the members

of the Committee resident in San Francisco. The work of the Resident Members has been assigned to different sub-committees, and Chairman Durand has made the following appointments:

EXECUTIVE COMMITTEE: W. F. Durand, *Chairman, ex-officio*; W. A. Cattell, *Secretary, ex-officio*; E. H. Benjamin, W. G. Dodd, A. M. Hunt.

FINANCE COMMITTEE: W. G. Dodd, *Chairman*; Newton Cleaveland, R. S. Moore.

PAPERS COMMITTEE: A. M. Hunt, *Chairman*; A. L. Adams, H. F. Bain, G. W. Dickie, W. R. Eckart, C. D. Marx, C. R. Weymouth.

PUBLICITY COMMITTEE: W. A. Cattell, *Chairman*; C. Derleth, Jr., W. S. Noyes, T. W. Ransom.

LOCAL AFFAIRS COMMITTEE: E. H. Benjamin, *Chairman*; J. G. De Remer, H. P. Frear.

The scope of the Congress has not as yet been definitely determined, but it is hoped to make it widely representative of the best engineering practice throughout the world, and it is intended that the papers, discussions and proceedings shall constitute an adequate review of the progress made during the past decade and an authoritative presentation of the latest developments and most approved practices in the various branches of engineering work.

The Committee of Management has extended a most cordial invitation to the officers and members of the American Chemical Society to attend and to participate in the proceedings of this Congress. The formal invitation, handsomely engraved, is now in the hands of Secretary Parsons and will be presented at the next meeting of the Council.

AMERICAN ENGINEERS ENTERTAINED IN GERMANY

Upon invitation of the Verein Deutscher Ingenieure, three hundred American engineers and their lady companions attended the Fifty-fourth Meeting at Leipzig, Germany. A tour of inspection throughout Germany was arranged for the foreign guests by the society.

WILLIAM JAMES EVANS

RESOLUTIONS BY THE CHEMISTS' CLUB

On the occasion of the death of William James Evans, the Board of Trustees of the Chemists' Club of New York City passed the following resolutions in token of their esteem and respect:

The Board of Trustees of the Chemists' Club, for itself and for the members of the Club, take this opportunity of recording its sorrow and regret at the passing of William James Evans, a member of the Board and former Treasurer.

The kindly and friendly interest which Mr. Evans took in the Club and all its functions, his sincere and cordial meeting with all its members, and his efficient and unflagging cooperation in forwarding the interests of the Club made him not only a member of unusual usefulness but also a warm, personal friend of each of us.

The Board of Trustees also takes this opportunity of extending to the family of Mr. Evans its sympathy in the affliction that has befallen them.

WALKER BOWMAN
B. C. HESSE
CHAS. BASKERVILLE
L. H. BAEKELAND
E. G. LOVE

Committee.

MINE SANITATION SECTION OF U. S. BUREAU OF MINES

The United States Bureau of Mines is about to investigate the conditions under which a miner works, believing that the unsanitary conditions which exist in some of the mines as well as in some of the mining towns are a factor in the death rate among the men. It is intimated that these conditions not only unnecessarily cause the death of miners through disease, but are often responsible for accidents which might not happen if the miners were in perfect health.

The Bureau has organized what is known as the Mine Sanitation Section, in charge of J. H. White, engineer.

NOTES AND CORRESPONDENCE

A CRITICISM OF CHEMICAL ABSTRACTS

Editor of the Journal of Industrial and Engineering Chemistry:

In the July number of *THIS JOURNAL*, in an editorial entitled "An Index to Chemical Literature," Dr. L. H. Baeke-land makes a criticism of *Chemical Abstracts* which has the appearance of being so serious that I feel some reply must be made to it.

He quotes from a report on the Patent Office in which the Government indexers state that they compared 6 pages of the index of the *Journal of the (London) Chemical Society* for 1909 with 1909 index of *Chemical Abstracts* and that out of 256 articles indexed in the former they failed to find 159 in *Chemical Abstracts*.

This certainly looks bad, and might lead the reader to conclude that *Chemical Abstracts* is not half covering the field.

I have gone minutely over three of the six pages referred to and find the following: Out of 125 articles indexed in the London index, only 4 have not been found in *Chemical Abstracts*.

One cause for failure to find entries is that in 1909 *Chemical Abstracts* was behind on many journals and struggling to catch up (*Chemical Abstracts* was only in its third year and just getting started); about 50 of the missing entries are to be found in the 1910 volume and so would eventually have come into the card index of the Patent Office. But the principal discrepancy is due to different methods of indexing. For instance, the London journal indexes aminoacetanilide under acetanilide, while

Chemical Abstracts indexes it under Am. The same applies to nitro and many other compounds. Furthermore, the English journal takes great liberties with the names of organic compounds as they appear in the article, renaming them if it thinks desirable. This has advantages and disadvantages; *Chemical Abstracts* has never done so much renaming.

This variance in indexing between the two journals only emphasizes, of course, the difficulties in the way of preparing a general index.

A letter received by us from Mr. W. F. Woolard, Chief Clerk of the Patent Office, says:

"It is probable that no two chemists, making this comparison, would exactly agree in the number of articles covered by one index and not mentioned in the other, without consulting the original monographs. Different abstractors will treat the same article from different view points, so that it becomes at times difficult to say whether or not an article has been abstracted by one journal and omitted by the other, without reference to and study of the original articles. For this detailed study there was neither time nor necessity in our investigation.

"The object which the office had in making this comparison was not with a view to criticism of the work of the American Society, but to ascertain whether subject matter appeared in the English work, which could not be found in the American in order to decide whether or not it was advisable to index both works."

It is evidently out of the question for *Chemical Abstracts* to index so minutely as to cover all the entries in the English index. We have already three times as many entries as it has, and it, as well as the index to *Chemisches Zentralblatt*, has, for some time, been regularly checked to see that no article is omitted. We do not pretend that of the articles in the 600 journals which we now have listed, all have been abstracted quickly. Many have been delayed and perhaps some missed altogether. Particular journals are constantly falling behind for various causes and it is a continual struggle to bring them up-to-date. Nevertheless, in 1909 the abstracting was not in the state that Dr. Baekeland's well-meant criticism might imply, and at the present time the material in nearly all departments is reaching us very promptly indeed.

AUSTIN M. PATTERSON

July 25, 1913

PAINTS FOR INDICATING THE USES OF PIPES

Editor of the Journal of Industrial and Engineering Chemistry:

I note with interest, THIS JOURNAL, p. 609, July, 1913, the extract of an article from *Engineering* that in 1911 German engineers "came to a preliminary understanding that it was desirable to paint pipes so as to avoid confusion, etc."

I do not know whether this practice was original with me, but I instituted it in the late fall of 1896, and at the same time instituted a method of painting barrels so as to be able to distinguish them at a glance. In 1903, when we built our present plant, the method of painting pipes was carried out to a nicety and color charts were distributed at various places so that every workman had the key to the colors. Every year that students in industrial chemistry visit our plant, the superintendent makes it a point to show the various colored pipes and their meaning.

My object in writing is, however, not to claim priority, although I never saw it anywhere until some years later I noticed it in one of our battleships. I wish, however, to point out that certain kinds of paint are better than others for this purpose. For instance, it is stated that steam pipes should be white. This is a mistake, because almost all white paints turn yellowish brown in time when subjected to continued heat. The varnish enamels of the Demar mastic type remain white but eventually become brittle and flake. At the same time, all steam pressure pipes excepting those used for heating are usually insulated with magnesia covering. In our plant we found that aluminum paint is ideal for all steam pipes whether covered or uncovered like exhaust pipes and this aluminum paint can be bought from any reputable manufacturer. It should be composed of a hard copal with plenty of diluent in it and must not be of the collodion type.

The other paints should be enamel paints and not oil paints. Enamel paints dry with a smooth gloss and do not take the dust readily. Oil paints take dust and are difficult to clean. Nothing is more obnoxious in a factory than a fine artistic layer of dust on the top and sides of painted pipe.

In addition to the enameling of pipes, we mark each one with a key number showing the contents.

This system is carried out in our works to other apparatus. For instance, we have about twenty eccentric rotary pumps for handling volatile and other liquids. These pumps are all enameled to correspond with the pipes and the chart. I mentioned the subject of barrels, and we paint all insulating and water-proof paint barrels one color and all oil-paint another color, so that there can never be a mistake in labeling them afterwards.

The color scheme is carried out in every department. The factory orders which come from the New York office are made out in quintuplicate of different colors. All stationery and instructions to the shipping office are on bright yellow paper. All manufacturing slips are blue, and so on. In this manner,

when a yellow order sheet is found in the manufacturing department it is at once easy to see that some one from the shipping department is there investigating the date when an order was filled. I could continue this, but it would take too much space. Suffice it to say that these small matters go a great way toward making a factory "fool-proof."

MAXIMILIAN TOCH

914 ST. AND WEST AVE.
LONG ISLAND CITY
August 5, 1913

ON METHODS OF ANALYSIS OF CRUDE GLYCERINE

Editor of the Journal of Industrial and Engineering Chemistry:

I wish to open a discussion on the present system of the analysis of crude glycerine, and would say at the outset that I believe there is an unhealthy condition existing somewhere. Let me mention a case, withholding the names. A sells two car loads of Soap Lye Crude to B, with C named as referee. A, upon careful analysis, finds 83.8 per cent Glycerol by the International Standard Method, and bills it accordingly. B reports that his chemists find 85.2 per cent Glycerol, but will split the difference. A has been very careful with his work (having been there before), and has his figures from two chemists, who are experienced in carrying out the International Standard Method. A, therefore, has a third portion of the sealed sample, taken by a public sampler, sent to C for analysis, requesting a detailed report, that he may check up the work of his chemists. In a few days the report comes in as follows:

	Per cent
Residue at 160° C.....	12.60
Water.....	5.4
Glycerol by the International Method.....	82.80
	82.85 Av. 82.87
	82.95
Correction for acetylatable impurities in the residue at 160° C.....	0.45
Anhydrous Glycerol.....	82.42

This is not a full report. According to the British Standard Specifications and Recommendations of the Executive Committee, the report should be as follows:

	Per cent
Total Acetyl Value as Glycerol.....	...
Acetyl Value (a) of Residue as Glycerol.....	...
Less Allowance.....	...
Correction for Acetyl Value of Residue as Glycerol.....	...
Glycerol (I. S. M., 1911).....	...
Ash.....	...
Organic Residue.....	...
Free Acid in terms of Na ₂ O.....	...
Alkali Hydroxide, and Carbonate, in terms of Na ₂ O.....	...

(a) Not determined if Total Organic Residue is 2.5 per cent or under in the case of Soap Lye Crude.

Note that in C's report there is no mention of Ash, Organic Residue, or Acetyl Value of Residue as Glycerol. By the correction, we take it for granted that Organic Residue was over 2.5 per cent, and that it was acetylated.

A, wishing to compare results more fully, wrote the referee asking for the percentage of Ash, Organic Residue at 160° C., and the Acetyl Value of the Residue as Glycerol. The reply was: "It is not customary to give a detailed report." Why? We pay for it. A insisted on a detailed report and the reply was as follows: "It is our custom in making the analysis of samples of Crude Glycerine to make those determinations which are necessary to enable us to report the total glycerol figure. For this reason the only determinations we make are

Total acetylatable matter in the sample as received.

Total residue at 160° C.

Acetylatable matter in the residue non-volatile at 160° C.

"Our customary charge for the above determinations is \$15, and when additional information is desired there is an additional charge."

Now how can C tell whether the non-volatile organic residue

at 160° C. is over 2.5 per cent unless they determine it, and how can it be found unless the Ash is determined? It is worthy of note that the report gives "Correction for Acetylizable impurities in the Residue non-volatile at 160° C. No mention is made of the Acetyl Value of the Residue nor of the Allowance. Was the Allowance made? The percentage of water is given, which is one of the most unsatisfactory of all tests, and which is not called for in the regular forms. Can you blame A for wondering if the International Standard Method was carried out at all, or feeling that he is being handed a gold brick?

One "Authority" (?) on the Analysis of Soap Lye Crude by the International Standard Method refuses to give anything but the final Glycerol Content. Let us study the three different results a moment. Is it likely that B or B's chemists are going to make errors against their interests by three-quarters of a per cent? Is it likely that A's chemists would both make an error of 1.38 per cent, knowing that their figures were sure to be checked? This is not an isolated case. I can cite others like it in every detail, in which other parties were concerned. What is the Answer? Do our leading chemists as referees, relying on their having the last word and their reputation, do careless work or leave the work to incompetent men? Do they carry out the International Standard Method according to specifications, and, if they do, WHY do they object to giving the result at every step? If such a report were given, then we poor unskilful chemists could check our work and find our errors. If we have a standard, let us live up to it.

One who knows writes that in cases of samples being referred to a referee, the reports are "almost always in favor of the buyer." Why? Is there no way to obtain satisfaction in the matter? If the work is done in order to reach the final figure, what objection can be raised to giving the figures according to the regular forms? I hope other chemists and soap-makers will take up the discussion and see if we can start something in the right direction.

E. A. RAY.

[I have in my possession a pound of the sealed sample (referred to above), taken by a public sampler, from the same mixture, and at the same time as were the other three samples, and am willing to submit a portion of it to anyone wishing to examine it.—E. A. R.]

MALDEN, MASS.
July 26 1913

WHAT'S THE MATTER WITH THE AMERICAN CHEMIST?

Editor of the Journal of Industrial and Engineering Chemistry:

I feel the need of expressing myself on some of the ideas put forth in the address of Mr. Daniel M. Grosh in *THIS JOURNAL*, 5, 692.

Years ago I was engaged with other chemists in promoting the development of the American dyestuff industry, by sitting comfortably in the laboratory and lamenting its comparative insignificance. In the midst of our lamentations the boss walked in and started things by remarking "Quit your tin-canning and get to work."

What is the use in celebrating the ability, the energy and efficiency of the American chemist and damning the manufacturer and capitalist?

The manufacturer and capitalist won't be convinced of the error of their ways, and their lost opportunities for fortune, by talk or printers' ink. They must be shown and they won't need any more showing than their German analogues, though, of course, Rene Bohn, for instance, will have less trouble in showing a German, than John Smith, A. C., will have in showing an American.

John Smith, A. C., is up against certain conditions that he must meet, and "tin-canning" isn't the best method of approach. If John Smith, A. C., has a job and will adapt himself to Amer-

ican manufacturing conditions, he can make good if he has anything to make good on. But if he is infected with *B. research tersanctus*—God help him.

Cords of good white paper and millions of cubic feet of air are used up annually in extolling research, but the average young chemist doesn't know what the word means. As nearly as I can judge, he thinks it means from \$1,500 to \$2,000 a year, a beautiful white laboratory, and plenty of time in which to read the morning paper and wait for inspiration. If he will realize that commercial research means a dollar sign and not a halo, and go to work on the problems that present themselves with the means at his disposal, or that can be obtained by the exercise of all his tact, he may know what research means after a year or two.

As the American dyestuff industry is generally taken as the "horrible example" in these lamentations, I hope to be allowed to state that a large number of useful dyes are made in this country and they are just as good as the same dyes of German make.

Furthermore, if John Smith, A. C., has any well-developed plan by which the American Coal Tar Color industry can be extended, I know where he can find all kinds of financial support for it. It should be understood, however, that while Rene Bohn can probably get backing for a test tube experiment, John Smith, A. C., will have to show something more.

W. H. WATKINS

BUFFALO, N. Y.
Aug. 8, 1913

WHAT'S THE MATTER WITH THE AMERICAN CHEMIST?

Editor of the Journal of Industrial and Engineering Chemistry:

In Mr. J. M. Matthews' reply to Mr. Grosh's article with the above title (*THIS JOURNAL*, 5, 626 and 692, respectively), he states that one of the main troubles with the American Chemist is that he wants real money for his services, truly a heinous condition, while his German colleague is willing to work on "prospects." We have heard the dogma preached from Wall Street for many years: "Young man, don't work for money. Work for experience and when you are old enough we will give you a nice little pension."

The trouble is not with the chemist but with the manufacturer. Instead of regarding his research chemist as a highly trained specialist, he regards him as a day laborer, makes him punch a time clock and thinks that if favorable results are not obtained immediately, the man is not worth his hire. Would he for one minute think of putting his physician on such a basis—*No Cure, No Pay?*

In the case of the physician or lawyer, even laymen can appreciate the difficulties with which he struggles, but the chemist battles only with "the innate perversity of inanimate things," and that, as we all know, is absurdly easy!

Of course, the manufacturer has had enough experience with "has-been," "would-be" and "analytical" chemists who pretended to be "research" chemists. It is this class who have puttered away the manufacturer's time, money and patience and prejudiced him against research. These "has-been" chemists, too, are always crying that there is a vast difference between laboratory and factory research.

There is only one kind of research, and that is research that brings results to the person who commands it. The skilled research chemist must have a large modicum of "horse-sense" which is acquired neither by experience nor association.

And after all, suppose a young chemist has worked for some time on "prospects" and finally has achieved something for a manufacturer. What guarantee has he that his work will be remunerated? Will there not be hundreds of new chemists waiting eagerly in the bread line for some manufacturer to let them work on prospects?

In a great many cases, having obtained the best products of a man's brain, there would be no further inducement for retaining him

BROADWAY AND 116TH ST.
NEW YORK CITY
AUGUST 16, 1913

SIDNEY BORN

A RAPID METHOD FOR THE DETERMINATION OF FAT IN ICE CREAM

Editor of the Journal of Industrial and Engineering Chemistry:

From time to time there have been published in various journals many methods for the rapid determination of fat in ice cream. I have tried them all. Some required special apparatus or expensive Babcock bottles with glass stopcocks attached. Others required the removal of added sugar. These usually gave results too low. None of them seemed to be entirely satisfactory. Therefore, I decided to try some experiments to meet the following requirements: Time for the complete test must not exceed 10 minutes. The Babcock centrifuge must be used because almost every ice cream factory can boast of that much of a laboratory. Babcock *milk* bottles should be used on account of finer graduations than cream bottles.

After trying various acids and mixtures in varying quantities, I finally hit upon the following simple modification of the Babcock test which does not char the sugar and meets all the requirements aforementioned.

Weigh into a 10 per cent Babcock *milk* bottle, 9 grams of melted sample. Add 20 cc. of glacial acetic acid (gravity 1.049). Mix well and add 10 cc. of sulfuric acid (gravity 1.83). Mix again and proceed as in the regular Babcock test. With the aid of a pair of dividers, read the fat column (from one extreme to the other, in other words read the highest part of the meniscus which appears as a straight line when bottle is held on the level of the eye and away from the source of light) at a temp. of 130° F. The result $\times 2$ = per cent fat.

I have used this method for about one year and have always obtained a clear straw-colored fat column free from any char or undissolved casein.

HOEFLER ICE CREAM CO.
BUFFALO, N. Y.
July 30, 1913

H. F. LICHTENBERG

PEAT POWDER AS FUEL FOR LOCOMOTIVES

Consul Douglas Jenkins, Goteborg, Sweden, reports that the recent announcement that Von Porat, a Swedish engineer, had perfected a process for utilizing peat powder as fuel for locomotives has awakened interest in the possibility of developing the extensive peat bogs of Sweden.

The powder is manufactured by the Ekelund process. A factory

has been in operation several years at Back Moss, Sweden, under the management of Mr. Herman Ekelund, inventor of the powder process. It does not appear that the process has made much headway as yet, but it is now predicted that in connection with the discovery of Mr. Von Porat, the use of peat powder will in time become extensive.

In the Von Porat system, the peat powder is fed by an automatic process into the furnace of the locomotive, which is specially arranged to consume it. The Ekelund process is on the market in various countries, including the United States, but little has been made public concerning the Von Porat method. According to Mr. Von Porat the results obtained with peat powder may be summed up as follows:

Substantially the same results can be had from 1½ tons of peat powder that 1 ton of coal will produce. Peat powder may be burned with an admixture of about 5 per cent of coal. As to firing with peat powder, the work is almost nothing in comparison with firing with coal, because the powder is forced into the furnace by an automatic process. No change had to be made in the boiler and none in the fire-box, except installing the special apparatus. There is no difficulty in bringing the powder from the tender to the fire-box, as it passes through a conveyance pipe. Another advantage in using peat powder is that no cold air can get into the fire-box and neither smoke nor sparks escape from the smokestack.

As a result of this invention, it is reported that a number of the Swedish railways are preparing to use peat powder instead of coal.

In view of the fact that the Von Porat appliances have not yet been patented, it is impossible to obtain any detailed description of his process or appliances.

THE CHEMICAL COMPOSITION OF COOKED VEGETABLE FOODS. PART III.—CORRECTION

In the article under the above title, *THIS JOURNAL*, 5, 653, the following changes should be made:

Page 654, first column, 10th line from bottom should read "— 48.92 per cent of solid" and the last line should be "— 10.9 per cent of solid matter."

Page 655, Table III, the heading over the first brace should be "Proximate analysis of the water-free substance."

KATHERINE I. WILLIAMS

PAPER FROM SEAWEED

A Liverpool newspaper states that an English chemist has succeeded in making paper from seaweed. The product is said to be fireproof, waterproof and odorless and is expected to have considerable effect on the present system of wrapping perishable goods for transport.

BOOK REVIEWS

Chemical Works. Their Design, Erection and Equipment.

By S. S. DYSON AND S. S. CLARKSON. 204 pp., 80 illustrations and nine plates. London: Scott, Greenwood and Son. New York: D. Van Nostrand Co. Price, \$7.50 net.

The very attractive title of this book is rather misleading. The general make-up of the book is good, especially the illustrations, but the subject matter is presented in a decidedly elementary and popular style. The eleven chapters include: choice of site, notes on construction, first principles in laying out of works, the power house, sulfuric, hydrochloric, and nitric acid plants, high explosives, sulfate of ammonia, and artificial manure plants, and the general plant. A rather long appendix treats of the English Alkali Works Regulation Act and general welfare work.

The authors state that their aim has been to present, in each chapter, a summary of sound practice in up-to-date construction, to give practical details and to deal with the subject of designing new works as it would be dealt with by a consulting chemical engineer.

There are many general statements, such as "The weight of lead, roughly speaking, is about eleven times that of water" and "..... cast iron is a substance which, in consequence of its varied composition and uncertain properties, it is most difficult to classify," etc., etc., and furthermore there is an absolute lack of cost tables. While the general idea and aim of the authors are excellent there is not enough new material presented to make the book of very much value, particularly in this country.

The authors have omitted modern American factory practice and that, together with the high price charged for the book, will prevent its wide-spread use.

R. K. MURPHY

The Materials Used in Sizing. By W. F. A. ERMEN. Published by D. Van Nostrand Co. 126 pp., 6 illustrations. Price, \$2.00.

The author has brought together, in book form, the subject matter of a course of lectures delivered in the summer session of the Manchester School of Technology in 1911 on "The Materials used in Sizing."

The scope of the book can be perhaps best understood by naming the various chapters into which the book is divided: Introduction, Chapter I, The Starches and other Agglutinants; Chapter II, Weighting Materials; Chapter III, Softening Ingredients; Chapter IV, Antiseptics; Chapter V, Analysis of Sized Warp and Cloth; Chapter VI, The Preparation of Normal Volumetric Solutions; Chapter VII, Tables.

The various sizing agents are considered as to their use, particular physical and chemical properties, tendering effect, tendency to mildew, etc., and such methods of analysis are given as are of value for the rapid evaluation of each particular sizing agent.

The various methods of analysis are considered more from the standpoint of rapidity than great exactness and are treated in an elementary way.

The book will be of some interest to the trained chemist, but its greatest value is that the factory foreman, with limited knowledge of chemistry, will be able to use the rapid tests of identification given.

OTTO KRESS

Fatty Foods, their Practical Examination. By E. RICHARDS BOLTON AND CECIL REVIS. Philadelphia: P. Blakiston's Son & Co., 1913. Small octavo, 371 pages. \$3.50 net.

The subtitle states this to be a handbook for the use of analytical and technical chemists. The point of view from which the book is written is further indicated by the following from the preface: "To the more humble investigator in this difficult field we desire to present the results of many years' experience, with the hope that methods and ideas which have brought success to the authors may enable him also to elucidate the problems with which he may have to grapple, though we cannot lay too much stress on the fact that scientific and skilled adulteration has sounded the death-knell of rough and ready methods of examination." The reader is rarely offered more than one method for any given purpose, is not told which methods are "official" either in the food or the drug industry, is not given the range of "constants" recorded in the literature, but only what the authors consider the usual limits, and is rarely given a reference to the original publication of either the methods or the data which are included in the book.

This willingness of the authors to assume so complete a control of the reader, both as to selection and detail of methods and interpretation of results, is the distinguishing feature of the book and makes it a significant expression of the authors' experience. On the other hand, the professional chemist, or even the reasonably advanced student, should know the sources of his methods and of the data which he uses in the interpretation of his results, and should have command of a considerable range of confirmatory methods. In this country it is important that he also know which methods have received "official" sanction for use in food and drug inspection, and that he be able to interpret his data in the light of "standards of purity" of the Association of Official Agricultural Chemists and of the United States Pharmacopoeia.

Those who have to do with the examination of fatty foods

should examine this work and profit by the ripe experience of its authors, but should use it in conjunction with other books, and not rely so exclusively upon it as the authors seem to contemplate.

The book is abundantly provided with good illustrations and its scope is somewhat broader than might be expected from its title, since it includes chapters on cocoa and chocolate, feeding-stuffs and milk. It may also be noted that the chapter on vegetable oils and fats covers many substances not primarily regarded as foods. The text is not strictly confined to analytical matters, but contains considerable information as to botanical and commercial sources and yields of the fats and oils described.

H. C. SHERMAN

Gasanalytische Methoden. VON WALTHER HEMPEL. Vierte Auflage, 1913. Friedrich Vieweg & Sohn, Brunswick \$3.00.

The fourth edition of Hempel's work on gas analysis contains considerable additional material; not much has been eliminated from the older book.

The chapter on sampling is essentially the same. Hempel's well-known gas analysis apparatus and pipettes, some of which are much used in this country, are again described. A form of absorption whereby only a small quantity of liquid is brought in contact with the gas sample is an addition. Hempel's apparatus for exact gas analysis without the use of rubber tubing connections between pipettes and the burette is again described. Although capable of giving exact results, the apparatus is probably used little or not at all in this country.

The Rotameter for measuring the flow of gases is described. Its limitations are not dwelt upon. Brief mention is made of the gas interferometer. This is another instrument which as yet has been little used in this country. For small amount of carbon dioxide, methane, etc., in air, it gives very accurate results.

The chapter on the purification of mercury remains essentially the same. An additional form of pipette for gas purification has been added.

The chapter on the combustion of gases has been enlarged.

A chapter has been added on the separation of gases by means of liquid air. Ramsey's and Travers' experiments are largely drawn upon.

The determination of dust in gas mixtures has been given attention.

The chapter on the determination of different gases is enlarged. Reference is made to Paul and Hartman's method whereby hydrogen is determined by absorption in palladium solution. The convenient Orsat is again described. Two gas balances are again described. It is questionable whether they are much used in this country. Some new material has been added to the chapter on coal gas. The chapter on atmospheric air remains good as in the other book.

Two forms of bomb calorimeter for the determination of the heating value of coal are described; also the Junker calorimeter for gases, and another one for which there is required only a small quantity of gas. A scheme for the determination of sulfur in organic material by combustion is again included. Hempel's gas lantern which he describes is not used in this country.

The book constitutes the same excellent treatise on gas analysis as the former editions of the work. Some of Hempel's apparatus are probably still more used in this country than other forms, although the tendency to-day is to install more one-piece or built up forms of apparatus, for convenience and speed. The book is very similar to that of L. M. Dennis recently issued. The latter has eliminated some parts that deal with methods in Hempel's book that are little used in this country.

GEORGE A. BURRELL

NEW PUBLICATIONS

By D. D. HEROLDZHEIMER, Librarian, Chemists' Club, New York

- Alkali Chlorides, The Electrolytic Decomposition of, with Stationary Cathodes.** Vol. II. JEAN HULLIER. 2 Vols. 8vo., pp. 180. Price, \$2.50. Wilhelm Knapp, Halle.
- American Electrochemical Society, Transactions.** XXIII, 1913. 8vo., pp. 432. American Electrochemical Society, South Bethlehem, Pa.
- Asphalts and Bitumens, Natural Rock.** A. DANBY. Cr. 8vo., pp. 284. Price, \$2.25. Constable & Co., London.
- Coal-Dust Explosion Tests, First Series of, in the Experimental Mine.** GEO. S. RICE, L. M. JONES, J. K. CLEMENT and W. L. EGY. 8vo., pp. 115. U. S. Bureau of Mines, Bulletin 56.
- Colloidal State of Matter.** L. CASSUTO. L. 8vo., pp. 252. Price, \$2.25. Dresden. (Translation into German.)
- Disinfection and Disinfectants.** M. CHRISTIAN. 8vo., pp. 112. Price, \$1.25. Scott, Greenwood & Co., London. (Translation.)
- Dyestuffs, The Synthetic, and the Intermediate Products from which they are Derived.** J. C. CAIN and J. F. THORPE. 2nd edition. 8vo., pp. 442. Price, \$4.00. C. Griffin & Co., London.
- Ethereal Oils, The. II.** GILDEMEISTER and HOFFMAN. 2nd edition. 8vo. Price, \$5.00. L. Staackmann, Leipzig. (German.)
- Gas, Analytical Methods for.** WALTHER HEMPEL. 4th edition. Price, \$3.00. Friedrich Vieweg & Sohn, Brunswick. (German.)
- Gas Engineers and Managers, Handbook for.** THOMAS NEWBIGGING. 8th edition. 8vo., pp. 578. Price, \$4.75. Walter King, London.
- Gas Manufacture, The Chemistry of.** H. M. RAYLE. 8vo., pp. 316. Price, \$4.50. A. M. Callender & Co., New York.
- Heat.** J. A. RANDALL. 8vo., pp. 345. Price, \$1.50. D. Van Nostrand Co., New York.
- Oil, Heavy, as Fuel for Internal Combustion Engines.** IRVING C. ALLEN. 8vo., pp. 36. U. S. Bureau of Mines, Technical Paper No. 37.
- Oil Industries, Chemistry of the.** J. E. DAUTHCOMBE. 8vo., pp. 209. Price, \$3.00. D. Van Nostrand Co., New York.
- Oils and Fats, Carbohydrate, Examination of.** D. HOLDE. 4th edition. 8vo., pp. 612. Price, \$4.50. Julius Springer, Berlin. (German.)
- Oils, The Volatile. Vol. I.** E. GILDEMEISTER. 2 vols. 2nd edition. 8vo., pp. 677. John Wiley & Sons, New York. (Translation.)
- Organic Chemistry, Yearbook of. VI (for 1912).** J. SCHMIDT. 8vo. Price, \$3.75. Johannes Woehrner, Leipzig. (German.)
- Organic Compounds, Chemical Technology of.** R. O. HERZOG. L. 8vo., pp. 732. Price, \$5.50. Heidelberg.
- Potassium Salts, The Occurrence of, in the Salines of the United States.** J. W. TURKENTINE. 8vo., pp. 96. U. S. Dept. of Agriculture, Bureau of Soils, Bulletin No. 94.
- Pumping and Hydraulic Machinery, Modern.** EDWARD BUTLER. 8vo., pp. 473. Price, \$4.50. Chas. Griffin & Co., London.
- Qualitative Analysis from the Ionic Standpoint.** W. BOETTGER. 3rd edition. 8vo. Wilhelm Engelmann, Leipzig.
- Rubber, The Chemistry of.** B. D. PORRITT. 8vo., pp. 96. Price, \$0.50. Gurney & Jackson, London.
- Steel, Its Selection, Annealing, Hardening and Tempering.** E. R. MARKHAM. 4th edition. Cr. 8vo. Price, \$2.75. Spon & Co., London.
- Sugar, Beet and Cane, Treatise on the Manufacture of. II.** DE GROBERT. 2 vols. 8vo. Price, \$12.00. J. Roussel, Paris.
- Water Purification and Sewage Disposal.** J. TILLMANN and H. S. TAYLOR. 8vo., pp. 143. Price, \$2.00. Constable & Co., London. (Translation.)
- 1898 to 1912.** By JOHN B. C. KERSHAW. *Chemical World*, Vol. 2, 1913, No. 7, pp. 228-232.
- Copper, The Metallography of Refined.** By EARL S. BARDWELL. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 79, pp. 1429-1441.
- Explosion of Gases, The Effect of Incombustible Dusts on the.** By H. B. DIXON and COLIN CAMPBELL. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 13, pp. 684-687.
- Gas, Coal, Decomposition of Carbon Bisulfide in, by Hot Purification.** By CHARLES CLAUDE CARPENTER. *Journal of Gas Lighting*, Vol. 123, 1913, No. 2616, pp. 30-33.
- Gases in Smelter Flues, Determination of.** By EDGAR M. DUNN. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 80, pp. 2051-2092.
- Indigo on Woolen Materials, Estimation of.** By A. G. GREEN, W. M. GARDNER, L. L. LLOYD and G. H. FRANK. *Textile Institute Journal*, Vol. 4, 1913, No. 1, pp. 16-42.
- Indigo, Synthetic, and its Derivatives.** By E. DE BARRY BARNITT. *Chemical World*, Vol. 2, 1913, No. 7, pp. 220-222.
- Oils, Lubricating.** By T. T. GRAY. *National Petroleum News*, Vol. 5, 1913, No. 3, pp. 36-41.
- Metals, Microstructure of.** By H. B. PULSIFER. *Chemical Engineer*, Vol. 17, 1913, No. 6, pp. 228-233.
- Nitric Acid from Ammonia, The Ostwald Process of Making.** ANONYMOUS. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 8, pp. 438-442.
- Oil Gas, Manufacture of.** By E. C. JONES. *Gas Age*, Vol. 32, 1913, No. 2, pp. 58-61.
- Oils, The Oxidation of.** By HARRY INGLE. *Paint, Oil and Drug Review*, Vol. 56, 1913, No. 6, pp. 19-21.
- Oil, Testing Lubricating.** By F. SCHWARZ and J. MARCUSSEN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 51, pp. 385-389.
- Ores, Concentration of Slimes at Anaconda, Mont.** By RALPH HAYDEN. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 80, pp. 1443-1467.
- Paints, Zinc, Lithopone and Lead.** By HENRY A. GARDNER. *Paint, Oil and Drug Review*, Vol. 56, 1913, No. 5, pp. 10-13.
- Petroleum, Chemistry and Technology of, during 1912.** By L. GURWITSCH. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 51, pp. 377-385.
- Petroleum, Fractionation of California, by Diffusion through Fuller's Earth.** By J. ELLIOTT GILPIN and P. SCHNEEBERGER. *American Chemical Journal*, Vol. 50, 1913, No. 2, pp. 59-100.
- Petroleum, The Optical Activity of, and its Significance.** By F. W. BUSHONG. *Science*, Vol. 38, 1913, No. 967, pp. 39-44.
- Petroleum Refining.** By COL. PRATT. *American Gas Light Journal*, Vol. 99, 1913, No. 2, pp. 27-28.
- Rubber Latexes, The Chemical Coagulation of.** By FREDERICK KAYE. *India Rubber Journal*, Vol. 45, 1913, No. 25, pp. 17-21.
- Rubber, Synthetic.** By E. STERN. *Chemiker Zeitung*, Vol. 37, 1913, No. 79, pp. 789-792.
- Smelting Copper Ores in the Electric Furnace.** By DORSEY A. LYON and ROBERT M. KEENEY. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 80, pp. 2117-2149.
- Steam, Economical Production and Use of.** By R. STANFIELD. *Journal of the Institute of Brewing*, Vol. 19, 1913, No. 5, pp. 361-368.
- Sulfate of Ammonia, The Walther Feld Process for the Manufacture of.** By A. PACCHIONI. *Journal of Gas Lighting and Water Supply*, Vol. 122, 1913, No. 2614, pp. 808-811.
- Sulfate Pulp Mills, The Waste Liquor from.** By W. O. WALKER. *Paper*, Vol. 11, 1913, No. 9, pp. 21-22 and 34.
- Sulfate Pulp, The Manufacture of.** By F. M. WILLIAMS. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 9, pp. 457-459.
- Sulfuric Acid Plant, Chamber Tests in a.** By E. H. ARMSTRONG. *American Fertilizer*, Vol. 38, 1913, No. 11, pp. 25-28.
- Tar and its By-products.** By S. R. CHURCH. *Gas Age*, Vol. 31, 1913, No. 10, pp. 497-501.
- Towers, Absorption and Reaction, for the Chemical Manufacturing Industry.** By RUDOLF HEINZ. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 57, pp. 419-422.
- Transmutation of Elements, Recent Work on the.** By A. T. CAMERON. *Radium*, Vol. 1, 1913, No. 3, pp. 3-5.
- Water Analysis for the Textile Industry, Methods of.** ANONYMOUS. *American Wool and Cotton Reporter*, Vol. 27, 1913, No. 28, pp. 857-858.
- Water Distilling Plant, Salt.** ANONYMOUS. *Lousiana Planter and Sugar Manufacturer*, Vol. 50, 1913, No. 22, pp. 347-351.
- Waterproofed Fabrics, Composition of.** By JOSEPH F. X. HAROLD. *Textile Manufacturers' Journal*, Vol. 21, 1913, No. 29, pp. 21

RECENT JOURNAL ARTICLES

- Air Filters.** By S. WILDING COLE. *Journal of the Institute of Brewing*, Vol. 19, 1913, No. 5, pp. 336-359.
- Aluminum Carbo-Nitrid.** By S. PEACOCK. *American Fertilizer*, Vol. 39, 1913, No. 3, pp. 25-29.
- Ammonia, Oxid of Iron Purification in Sulfate of, Works.** ANONYMOUS. *Journal of Gas Lighting*, Vol. 123, 1913, No. 2619, pp. 238-245.
- Arsenic and Antimony in Converter and Electrolytic Copper, The Determination of.** By E. E. BROWN. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 80, pp. 1489-1495.
- Arsenic Trioxide from Flue Dust.** By JAMES O. ELTON. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 80, pp. 1497-1509.
- Brass Analysis.** By BERTHOLD KOCH. *Chemiker Zeitung*, Vol. 37, 1913, No. 87, pp. 873-874.
- Coke Oven Carbonization.** By W. CHANEY. *American Gas Light Journal*, Vol. 99, 1913, No. 2, pp. 17-21.
- Coke Oven Plant, the Modern By-product, Recovery of By-products in.** By C. A. MEISSNER. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 8, pp. 454-458.
- Combustion, Flameless Surface.** By FRITZ KRULL. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 55, pp. 401-404.
- Copper Mining Industry, Development of the World's, in the Years**

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Precipitation of Material from Cyanid Solutions. C. W. Merrill, June 3, 1913. U. S. Pat. 1,063,569. The solution is passed through a comminuting apparatus in which it is brought in contact with a precipitant of the metals in solution having an inert non-metallic abrasive substance incorporated therewith.

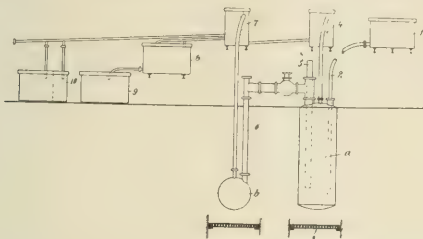
Bleaching Vegetable Fiber and Fabrics. R. Gruter, June 3, 1913. U. S. Pat. 1,063,678. The fibers or fabrics to be bleached are saturated with a hot solution of hydrogen peroxide; after removing the excess of the solution from the material it is exposed to heated ammonia vapors.

Refining Brown Sugar. Lundgren and Gierling, June 3, 1913. U. S. Pat. 1,063,708. A sugar solution of a density of 20° Baume is subjected to the action of ozone or ozonized air.

Preparing Hydrogenized Products from Unsaturated Compounds. A. Skita, June 3, 1913. U. S. Pat. 1,063,746. The hydrogenation is effected by the action of hydrogen in the presence of a small amount of a dissolved palladium salt.

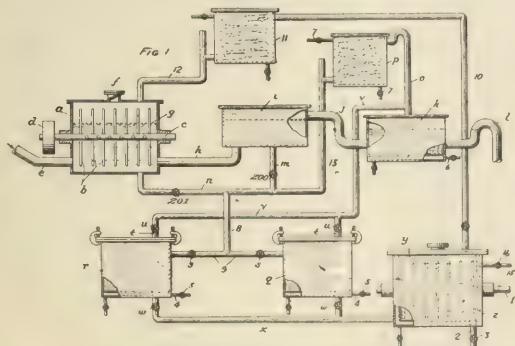
Magnetic Separation of Ores out of Slime. B. Schwerin, June 3, 1913. U. S. Pat. 1,063,893. The slimes are brought into a colloidal state and subjected to magnetic separation, with or without the addition of an electrolyte.

Production of Coke from Wood-Tar. F. W. Lefelmann, June 10, 1913. U. S. Pat. 1,064,350. The tar is first heated in a retort, *a*, to about 225° C. until constituents volatile at this temperature are driven off and condensed in condenser 4. The



residue is then heated to a high temperature and, having a tendency to foam, it boils over through siphon 6 into retort *b* where it is immediately exposed to a temperature of 400° C. or above and is coked without further foaming.

Production of Bromin or Bromids. F. I. du Pont, June 10, 1913. U. S. Pat. 1,064,460. Brine, containing the usual small content of bromin, is first electrolyzed to set free the bromin.



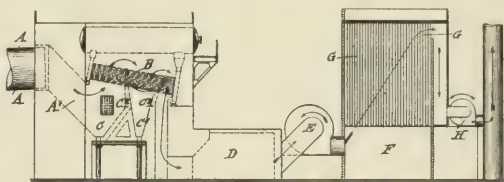
The bromin is extracted from the brine by means of a liquid

substantially insoluble in the brine and having a greater avidity for the bromin than the brine, such as carbon tetrachlorid. The mixture is allowed to stand until the carbon tetrachlorid collects in the bottom of the vessel from which it is drawn off.

The carbon tetrachlorid with its bromin content is subjected to the action of a water-absorbing reagent such as calcium chlorid which leaves the bromin and its solvent free from water.

The carbon tetrachlorid with the bromin therein is then agitated in the presence of some reagent as antimony, which will combine with the bromin. The mixture is then subjected to heat to drive off the carbon tetrachlorid.

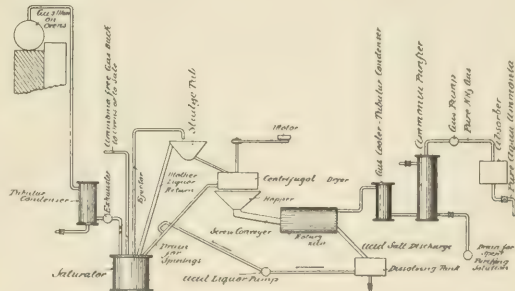
Utilizing Waste Gases of Combustion from Portland Cement, Lime and other Kilns. F. Schott, June 10, 1913. U. S. Pat. 1,064,550. The waste gases from the kiln *A* are passed through a steam boiler, *B*, and are therein cooled to a temperature of from 200° to 250° C. The coarser particles of dust are collected in receptacles *C* and *C'*.



The waste gases are then drawn by a fan or blower, *E*, through the cooling chamber *D*, where they are cooled below 100° C. and are forced through the filtering chamber *F* where the fine dust and potassium and ammonia salts are collected. The purified gases are drawn off by the fan or blower *H* and discharged into the chimney.

Steel, Iron, Etc. A. W. Machlet, June 24, 1913. U. S. Pat. 1,065,379. The steel is exposed to a temperature above 900° F. but below the melting point of steel, in an atmosphere of ammonia.

Obtaining Purified Ammonia from Coal Gas. C. G. Tufts, June 24, 1913. U. S. Pat. 1,065,566. In this process the oven



gases are directly treated to recover purified ammonia without the usual preliminary steps of washing and forming ammoniacal liquor.

The oven gases are passed through a saturator containing sulfuric acid or acid sulfate of ammonia. The ammonia combines with the acid to form ammonium sulfate.

The combined gases are drawn off leaving the ammonia, together with the remaining impurities, in the sulfate.

This is quickly heated to drive off the ammonia with the accompanying volatile impurities and the ammonia is finally separated from these impurities

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF AUGUST, 1913

ORGANIC CHEMICALS

Acetanilid.....	Lb.	21	@	23
Acetic Acid (28 per cent).....	C.	2.00	@	2.15
Acetone (drums).....	Lb.	15 ³ / ₄	@	16 ¹ / ₄
Alcohol, denatured (180 proof).....	Gal.	36	@	3 ¹ / ₂
Alcohol, grain (188 proof).....	Gal.	2.46	@	2.48
Alcohol, wood (95 per cent).....	Gal.	45	@	47
Amyl Acetate.....	Gal.	2.20	@	2.30
Aniline Oil.....	Lb.	10 ¹ / ₈	@	10 ³ / ₈
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	21	@	23
Camphor (refined in bulk).....	Lb.	42 ¹ / ₂	@	44
Carbolic Acid (drums).....	Lb.	9 ³ / ₄	@	13
Carbon Bisulfide.....	Lb.	6 ¹ / ₂	@	8
Carbon Tetrachloride (drums).....	Lb.	7 ³ / ₄	@	8 ¹ / ₄
Chloroform.....	Lb.	25	@	35
Citric Acid (domestic), crystals.....	Lb.	46 ¹ / ₂	@	47
Dextrine (corn).....	C.	3.12	@	3.75
Dextrine (imported potato).....	Lb.	6	@	7
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	8 ¹ / ₂	@	9 ¹ / ₂
Glycerine (dynamite).....	Lb.	18 ¹ / ₄	@	19
Oxalic Acid.....	Lb.	7 ¹ / ₈	@	8
Pyrogalllic Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	28	@	30
Starch (cassava).....	Lb.	3 ¹ / ₄	@	4
Starch (corn).....	C.	2.34	@	3.00
Starch (potato).....	Lb.	4 ¹ / ₂	@	5
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	2 ³ / ₄	@	2 ³ / ₄
Starch (wheat).....	Lb.	5	@	6 ¹ / ₂
Tannic Acid (commercial).....	Lb.	35	@	36
Tartaric Acid, crystals.....	Lb.	30 ¹ / ₄	@	30 ¹ / ₄

INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 ³ / ₄	@	8
Acetate of Lime (gray).....	C.	2.50	@	2.60
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 ¹ / ₂
Ammonium Chloride, gray.....	Lb.	6 ¹ / ₄	@	6 ¹ / ₄
Aqua Ammonia (drums) 16°.....	Lb.	2 ¹ / ₄	@	2 ¹ / ₂
Arsenic, white.....	Lb.	3.35	@	3.60
Barium Chloride.....	C.	1.60	@	1.80
Barium Nitrate.....	Lb.	5 ¹ / ₄	@	5 ¹ / ₂
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.20	@	1.25
Blue Vitriol.....	Lb.	5	@	5 ¹ / ₄
Borax, crystals (bags).....	Lb.	3 ³ / ₄	@	4 ¹ / ₄
Boric Acid, crystals (powd.).....	Lb.	7	@	7 ¹ / ₂
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	85	@	1.10
Chalk (light precipitated).....	Lb.	4	@	4 ¹ / ₂
China Clay (imported).....	Ton	11.50	@	18.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.05	@	3.10
Lead Nitrate.....	Lb.	8 ¹ / ₄	@	8 ¹ / ₂
Litharge (American).....	Lb.	6 ¹ / ₂	@	7
Lithium Carbonate.....	Lb.	65	@	70
Magnesia (powdered).....	Lb.	5 ¹ / ₂	@	6
Magnesite (raw).....	Ton	30.00	@	31.00
Nitric Acid, 36°.....	Lb.	3 ⁷ / ₈	@	4 ¹ / ₄
Phosphoric Acid (sp. gr. 1.75).....	Lb.	21 ¹ / ₄	@	25 ¹ / ₂
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 ³ / ₄	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined) 80 @ 85%.....	C.	3.40	@	3.65
Potassium Chlorate, crystals.....	Lb.	8 ¹ / ₄	@	9 ¹ / ₂
Potassium Cyanide (bulk) 98-99%.....	Lb.	19	@	24
Potassium Hydroxide.....	C.	3.00	@	4.75
Potassium Iodide (bulk).....	Lb.	2.60	@	2.65
Potassium Nitrate (crude).....	Lb.	4 ¹ / ₄	@	5
Potassium Permanganate (bulk).....	Lb.	9 ¹ / ₂	@	11
Quicksilver, Flask.....	Lb.	40.00	@	—
Red Lead (American).....	Lb.	6 ¹ / ₂	@	7
Salt Cake (glass-makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	37 ¹ / ₂	@	39 ¹ / ₂
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	65	@	70
Sodium Acetate.....	Lb.	4	@	4 ¹ / ₂
Sodium Bicarbonate (domestic).....	Lb.	1.50	@	1.80
Sodium Bicarbonate (English).....	Lb.	2 ³ / ₄	@	3
Sodium Bichromate.....	Lb.	4 ¹ / ₂	@	4 ⁷ / ₈
Sodium Carbonate (dry).....	Lb.	60	@	80
Sodium Chlorate.....	Lb.	8 ¹ / ₄	@	9 ¹ / ₂
Sodium Hydroxide, 60 per cent.....	C.	1.57 ¹ / ₂	@	1.62 ¹ / ₂
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	2.35	@	2.40
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	6 ⁷ / ₈	@	7 ⁵ / ₈
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	11 ¹ / ₄	@	12
Tin Oxide.....	Lb.	44	@	46
White Lead (American, dry).....	Lb.	5 ¹ / ₄	@	6
Zinc Carbonate.....	Lb.	9	@	10
Zinc Chloride (granulated).....	Lb.	4 ¹ / ₂	@	5
Zinc Oxide (American process).....	Lb.	5 ³ / ₈	@	6 ³ / ₈
Zinc Sulfate.....	Lb.	2 ¹ / ₄	@	2 ³ / ₄

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	42	@	45
Black Mineral Oil, 29 gravity.....	Gal.	13 ¹ / ₂	@	14
Castor Oil (No. 3).....	Lb.	8 ⁷ / ₈	@	10
Ceresin (yellow).....	Lb.	12	@	12
Corn Oil.....	C.	6.65	@	6.70
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	—	@	—
Cottonseed Oil (p. s. y.).....	Lb.	8 ¹ / ₂	@	9 ¹ / ₂
Cylinder Oil (light, filtered).....	Gal.	21 ¹ / ₂	@	32
Japan Wax.....	Lb.	9	@	9 ¹ / ₂
Lard Oil (prime winter).....	Gal.	95	@	97
Linseed Oil (double-boiled).....	Gal.	54	@	55
Menhaden Oil (crude).....	Gal.	29	@	30
Neatsfoot Oil (20°).....	Gal.	98	@	1.10
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 ¹ / ₂	@	3 ³ / ₄
Paraffine Oil (high viscosity).....	Gal.	26	@	28
Rosin ("F" grade).....	Bbl.	4.40	@	4.45
Rosin Oil (first run).....	Gal.	30	@	34
Shellac, T. N.....	Lb.	23	@	23 ¹ / ₂
Spermaceti (cake).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	11
Tallow (acidless).....	Gal.	63	@	65
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	39 ¹ / ₂	@	40

METALS

Aluminum (No. 1 ingots).....	Lb.	22 ¹ / ₂	@	23
Antimony (Hallet's).....	Lb.	7 ³ / ₄	@	8 ¹ / ₂
Bismuth (New York).....	Lb.	2.10	@	2.15
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	Lb.	15 ¹ / ₈	@	16
Copper (lake).....	Lb.	15 ³ / ₄	@	16 ¹ / ₄
Lead, N. Y.....	Lb.	4.75	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	46.00	@	—
Silver.....	Oz.	59 ¹ / ₈	@	60
Tin.....	C.	40.00	@	44.00
Zinc.....	Lb.	5.70	@	5.80

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	3.00	@	—
Blood, dried.....	Unit	—	@	2.80
Bone, 4 ¹ / ₂ and 50, ground, raw.....	Ton	27.50	@	28.00
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.10
Castor meal.....	Unit	—	@	3.00
Fish Scrap, domestic, dried.....	Unit	2.75	@	10
Mowrah meal.....	Ton	—	@	nominal
Phosphate, acid, 16 per cent bulk.....	Ton	6.75	@	7.00
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	3.00	@	3.25
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	38.55	@	—
Pyrites, furnace size, imported.....	Unit	—	@	0.13 ¹ / ₂
Tankage, high-grade.....	Unit	2.72 ¹ / ₂	@	2.75 & 10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

OCTOBER, 1913

No. 10

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly.

Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

The Annual Meeting at Rochester.....	792	The Beckton Gas Light and Coke Company of London, England.....	862
Presidential Address: Industrial Research in America..	793	The Modern By-Product Coke Oven.....	862
ORIGINAL PAPERS:		"Neradol D," A Synthetic Tannin.....	863
Design of Surface Combustion Appliances. By Charles Edward Lucke.....	801	The Causes and Prevention of Sewer Pipe Failures.....	863
Methods for the Examination of Natural Gas for the Production of Gasoline. By E. S. Merriam and J. A. Birchby.....	824	A New Design in Boiler Settings.....	864
The Chemistry of Anaesthetics, V.; Ethyl Chloride. By Charles Baskerville and W. A. Hamor.....	828	A Separator for Dry Material.....	864
A Rapid Volumetric Method for Determining <i>o</i> -, <i>m</i> -, and <i>p</i> -Cresols, Thymol and Phenol. By L. V. Redman, A. J. Weith and F. P. Brock.....	831	Absorption and Reaction Towers for Chemical Works.....	865
An Apparatus and Method for Determining Hydrogen Sulfide in Illuminating Gas. By E. P. Harding and Einer Johnson.....	836	The Rotameter.....	865
A Method for the Determination of Phosphorus in Vanadium Steel and Ferrovanadium. By C. F. Sidener and P. M. Skartvedt.....	838	An Automatic Electric Drying Oven.....	866
A Fusion Method for the Determination of Sulfur in Iron and Steel. By Frederick H. Franklin.....	839	The Mineral Production of Sweden.....	866
The Analysis of Alloys of Lead, Tin, Antimony and Copper. By D. J. Demorest.....	842	The Production of Calcium Carbide.....	866
A Rapid and Accurate Gravimetric Method for Determining Fat in Ice Creams, Cereals and Chocolate. By E. P. Harding and Guy Parkin.....	843	Progress of the Electric Steel Industry.....	866
Proposed Method for Detecting Adulteration of Cider Vinegar with Distilled Vinegar. By S. L. Crawford.....	845	Iron Castings to Resist Corrosion.....	867
Chemical Studies on the Lime Sulfur-Lead Arsenate Spray Mixture. By W. E. Ruth.....	847	The Production of Finished Steel in 1912.....	867
Sponges as a Fertilizer. By Joseph G. Smith.....	850	The Composition of Water Gas.....	867
LABORATORY AND PLANT:		The Paper Industry of Austria-Hungary.....	867
The Chemical Laboratory of the Picher Lead Co. By John A. Schaeffer.....	850	SCIENTIFIC SOCIETIES:	
A Simple Gasoline Gas Generator for Sulfur Determinations. By C. E. Waters.....	853	American Chemical Society—Forty-eighth Meeting, Rochester.....	868
ADDRESSES:		American Electrochemical Society. Denver Meeting..	870
The Patent Expert and the Chemical Manufacturer. By Bernhard C. Hesse.....	854	The Chemical Societies in New York City.....	870
The Theory of the Removal of Suspended Matter from Gases. By W. W. Strong.....	858	Obituary—Eugene A. Byrnes.....	870
The Utilization of Sewage. By George A. Soper.....	860	Obituary—F. H. Daniels.....	871
CURRENT INDUSTRIAL NEWS:		NOTES AND CORRESPONDENCE:	
The Status of the Cement Industry.....	861	On Methods of Analysis of Crude Glycerine.....	871
		What's the Matter with the American Chemist.....	871
		On Calculating the Fat-Free Residue of Milk.....	872
		Note on Colorimetric Method for Titanium in Iron and Steel.....	872
		Petroleum Production in 1912.....	872
		Government Control of Chilean Mineral Deposits.....	873
		Scottish Oil Fuel for British Navy.....	873
		Progress of Artificial-Silk Industry.....	873
		Clay Products Industries in the United States in 1912..	874
		BOOK REVIEWS:	
		Iron and Steel; Metallic Alloys; Their Structure and Constitution; Service Chemistry; Liquid Air—Oxygen—Nitrogen; Disinfection and Disinfectants.....	874
		NEW PUBLICATIONS.....	877
		RECENT INVENTIONS.....	878
		MARKET REPORT.....	880

THE ANNUAL MEETING AT ROCHESTER

The Forty-eighth Annual Meeting of the American Chemical Society was held in Rochester, New York, September 8th to 14th. This is the first meeting held in the fall of the year under the newly adopted constitution, and is by far the most successful in the history of the Society. The large and representative attendance amply justifies the change in date for the annual meeting from the Christmas holidays to the fall of the year.

We publish elsewhere in this issue the program of papers presented to the general meetings and the various sectional meetings, and a study of the list will show an unusual number of valuable contributions to theoretical and applied chemistry. The greater portion of the papers in this program will be published in full in the Journals of the Society.

President Little's address was given on Wednesday morning at a general meeting in the East High School. The Sectional meetings were held in the Eastman Building, University of Rochester. The presidential address, which follows in full, is a most authentic and comprehensive treatment of the subject of Industrial Research in America, and its statements of the extent and thoroughness of this development in our more progressive industries will be a surprise to many of our readers. A careful reading of this address will undoubtedly suggest to delinquent American manufacturers that serious and genuine Industrial Research will offer the only means by which they may avoid the otherwise inevitable steam roller of crumbling tariff walls, foreign competition and antiquated methods and products.

The general meeting of the Society on September 9th was preceded by a meeting of the Board of Directors at the Hotel Seneca on Monday afternoon. The Rochester Section of the Society entertained the Council at dinner on Monday evening, after which the formal meeting of the Council was called to order by President Little. Dr. Chas. L. Parsons was elected Secretary of the Society and Dr. A. P. Hallock, Treasurer for a period of three years under the new constitution. The editors and editorial boards of the Society's journals were reelected for the current year, and the editorial staff of the *Industrial Journal* was strengthened by the addition of two assistant editorships.

The first general session was held in the Assembly Hall of the Eastman Kodak Company plant at Kodak Park, on Tuesday morning, and was opened by a cordial address of welcome by Mayor Edgerton. Papers were presented by Messrs. J. O. Handy, C. E. K. Mees, B. C. Hesse, G. A. Soper and Henry Leffmann.

At the conclusion of the morning session, the members and their guests were entertained at luncheon by the Eastman Kodak Company. After luncheon the manufacturing departments and laboratories of the plant were thrown open to inspection, and under the guidance of the technical members of the Eastman staff the visitors were given an excellent opportunity

to see one of the most highly developed industries in America.

The Rochester Section entertained the visiting members on Tuesday evening, at a smoker in Masonic Hall. The Entertainment Committee, under the direction of M. H. Eisenhart, ably assisted by large committees from the Rochester Section, provided a most elaborate program and feast for this occasion. Each guest was decked out in a commodious white apron, on which was inscribed, in bold letters, his name and address, and, as a protection against draughts a Chinese mandarin cap with pigtail. The liquid refreshments were provided in the form of a special brew supplied by the Moerback Brewery. The Smoker program was arranged with great care and consisted of selections by professional talent interspersed with much music from an orchestra, songs from a membership quartet, unusually interesting and instructive moving pictures, and several impromptu parades by guests. The entire function was most thoroughly organized and executed and will stand as a monument to the skill and energy of the Rochester Section.

The annual banquet was set for Thursday night at Powers Hotel. Dr. L. H. Baekeland acted as toastmaster and the principal speakers were President Rees of the University of Rochester; Edward W. Morley, past honorary president of the Eighth International Congress; President A. D. Little; H. E. Howe of Bausch & Lomb Optical Co.; C. H. Herty of the University of North Carolina; S. L. Bigelow of Washington; and Secretary C. L. Parsons. A delightful feature of the banquet was the orchestral music and a number of soprano solos.

The excursions to the plants of the Bausch & Lomb Optical Company, Taylor Instrument Company, Curttice Bros. Company, J. Hungerford Smith Company, Moerback Brewery, German-American Button Company, Genessee Reduction Company, Municipal Incinerator, Stecker Lithographic Company, and others, under the general direction of Mr. J. E. Woodland, Chairman of the Factory Excursions Committee, proved to be one of the most important features of the Annual Meeting. Rochester, being an industrial center, is admirably situated to provide this interesting and instructive feature of the program.

The Entertainment Committee had also made ample provision for the entertainment of the lady members and visitors in the form of a reception at the University Club, a card party at the Century Club, an excursion to Irondequoit Bay with luncheon at the Newport House and numerous automobile excursions through the city and neighborhood of Rochester.

The success of the meeting is due to the work of the local committees and it was the unanimous opinion of the visiting members that to the Rochester Section belongs the credit of organizing and administering to the minutest detail the innumerable features which contributed to the complete success of the Forty-eighth Annual Meeting.

INDUSTRIAL RESEARCH IN AMERICA

PRESIDENTIAL ADDRESS

By ARTHUR D. LITTLE

Germany has long been recognized as preeminently the country of organized research. The spirit of research is there imminent throughout the entire social structure. This is not the time nor place, however, nor is it necessary before this audience, to refer in any detail to the long record of splendid achievement made by German research during the last fifty years. It is inscribed in luminous letters around the rock upon which Germany now stands secure among the nations of the world.

The virility and range of German research were never greater than they are to-day. Never before have the superb energy and calculated audacity of German technical directors and German financiers transformed so quickly and so surely the triumphs of the laboratory into industrial conquests. Never has the future held richer promise of orderly and sustained progress, and yet the preeminence of Germany in industrial research is by no means indefinitely assured. A new competitor is even now girding up his loins and training for the race, and that competitor is strangely enough the United States—that prodigal among nations, still justly stigmatized as the most wasteful, careless and improvident of them all.

To one at all familiar with the disdain of scientific teaching which has characterized our industry, and which still persists in many quarters, this statement is so contrary to the current estimate that its general acceptance cannot be expected. It will have served its purpose if it leads to a consideration of the facts which prove the thesis.

The country of Franklin, Morse and Rumford; of McCormick, Howe and Whitney; of Edison, Thomson, Westinghouse and Bell; and of Wilbur and Orville

Wright, is obviously a country not wholly hostile to industrial research or unable to apply it to good purpose. It is, however, not surprising that with vast areas of virgin soil of which a share might be had for the asking; with interminable stretches of stately forest; with coal and oil and gas, the ores of metals and countless other gifts of nature scattered broadcast by her lavish hand, our people entered upon this rich inheritance with the spirit of the spendthrift, and gave little heed to refinements in methods of production and less to minimizing waste. That day and generation is gone.

Today, their children, partly through better recognition of potential values, but mainly by the pressure of a greatly increased population and the stress of competition among themselves and in the markets of the world, are rapidly acquiring the knowledge that efficiency of production is a sounder basis for prosperity than mere volume of product, however great. Many of them have already learned that the most profitable output of their plant is that resulting from the catalysis of raw materials by brains. A far larger number are still ignorant of these fundamental truths, and so it happens that most of our industrial effort still proceeds under the guidance of empiricism with a happy disregard of basic principles. A native ingenuity often brings it to a sur-

prising success and seems to support the aphorism "Where ignorance is profitable, 'tis folly to be wise." Whatever may be said, therefore, of industrial research in America at this time is said of a babe still in the cradle but which has nevertheless, like the infant Hercules, already destroyed its serpents and given promise of its performance at man's estate.

The long-continued and highly organized research which resulted in the development of American agricultural machinery has led to the general introduction of machines which reduce the labor cost of seven



PRESIDENT LITTLE

crops \$681,000,000 as measured by the methods of only fifty years ago.

The superhuman dexterity and precision of American shoe machinery, which has revolutionized a basic industry and reduced competition to the status of an academic question, present American industrial research at its best. They are not the result of the individual inspiration of a few inventors as is commonly supposed. They represent years of coördinated effort by many minds directed and sustained by constant and refined experimental research.

You need not be reminded that the ubiquitous telephone is wholly a product of American research. Munchausen's story of the frozen conversation which afterward thawed out is a clumsy fable. Think of the Niagaras of speech pouring silently through the New York telephone exchanges where they are sorted out, given a new direction and delivered audibly perhaps a thousand miles away. New York has 450,000 instruments—twice the number of those in London. Los Angeles has a telephone to every four inhabitants. Why should one care to project one's astral body when he can call up from the Club in fifteen seconds? Our whole social structure has been reorganized, we have been brought together in a single parlor for conversation and to conduct affairs because the American Telephone and Telegraph Company spends annually for research, the results of which are all about us, a sum greater than the total income of many universities.

The name of Edison is a household word in every language. The Edison method is a synonym for specialized, intense research which knows no rest until everything has been tried. Because of that method and the unique genius which directs its application, Italian operas are heard amid Alaskan snows and in the depths of African forests; every phase of life and movement of interest throughout the world is caught, registered, transported and reproduced that we may have lion hunts in our drawing-rooms and the coronation in a five-cent theatre. From his laboratory have come the incandescent lamp, multiple telegraphy, new methods of treating ores and a thousand other diverse inventions, the development of a single one of which has sometimes involved millions.

The development of the automobile, and especially of the low-priced American car, is a thing of yesterday. To-day a single manufacturer turns out two cars a minute, while another is expanding his output to 500 cars a day. Every 23 days the total engine horsepower of new cars of one small type equals the energy of the entire Mississippi river development at Keokuk. Every 46 days this engine output rises to the total energy development at Niagara Falls. The amount of gasoline consumed upon our roads is equal to the water supply of a town of 40,000 inhabitants, and its cost on Sundays and holidays is \$1,000,000.

It goes without saying that any such development as that of the automobile industry in America has been based upon and vitalized by an immeasurable amount of research, the range and influence of which extends through many other industries. It has accelerated the application of heat treatment more than

any other agency. One tire manufacturer spends \$100,000 a year upon his laboratory. The research department organized by my associates for one automobile company comprised within its staff experts in automobile design, mathematics, metallography and heat treatments, lubrication, gaseous fuels, steel and alloys, paints and painting practice, in addition to the chemists, physicists and assistants for routine or special work.

The beautiful city whose hospitality has so greatly added to the pleasure and success of the present meeting of our Society is the home of two highly scientific industries of which any community may well be proud. The Bausch & Lomb Optical Company, through its close affiliation with the world-famed Zeiss works at Jena, renders immediately available in this country the latest results of German optical research. The Eastman Kodak Company is perhaps more generally and widely known than even the Zeiss works, and in capital, organization, value of product and profit of operation will bear comparison with the great German companies whose business is applied science. Like them, it spends money with a lavish hand for the promotion of technical research and for the fundamental investigation of the scientific bases on which its industry rests. As you have happily been made aware, this work is carried on in the superb new research laboratories of the company with an equipment which is probably unrivalled anywhere for its special purposes. The laboratory exemplifies a notable feature of American industrial research laboratories in that it makes provision for developing new processes first on the laboratory scale and then on the miniature factory scale.

To no chapter in the history of industrial research can Americans turn with greater pride than to the one which contains the epic of the electrochemical development at Niagara Falls. It starts with the wonderful story of aluminum. Discovered in Germany in 1828 by Wöhler, it cost in 1855, \$90 a pound. In 1886, it had fallen to \$12. The American Castner process brought the price in 1889 to \$4. Even at this figure it was obviously still a metal of luxury with few industrial applications. Hall in America and Héroult, simultaneously in Europe discovered that cryolite, a double fluoride of sodium and aluminum, fused readily at a moderate temperature, and when so fused dissolved alumina as boiling water dissolves sugar or salt, and to the extent of more than 25 per cent. By electrolyzing the fused solution aluminum is obtained. On August 26, 1895, the Niagara works of the Pittsburgh Reduction Co., started at Niagara Falls the manufacture of aluminum under the Hall patents. In 1911, the market price of the metal was 22 cents and the total annual production 40,000,000 pounds.

A chance remark of Dr. George F. Kunz, in 1880, on the industrial value of abrasives, turned the thoughts of Acheson to the problem of their artificial production and led to the discovery, in 1891, of carborundum and its subsequent manufacture on a small scale at Monongahela City, Pennsylvania. In 1894, Acheson laid

before his directors a scheme for moving to Niagara Falls, when to quote his own words:

"To build a plant for one thousand horse-power, in view of the fact that we were selling only one-half of the output from a one hundred and thirty-four horse-power plant, was a trifle too much for my conservative directors, and they, one and all, resigned. Fortunately, I was in control of the destiny of the Carborundum Company. I organized a new board, proceeded with my plans, and in the year 1904, the thirteenth from the date of the discovery, had a plant equipped with a five-thousand electrical horse-power and produced over 7,000,000 pounds of those specks I had picked off the end of the electric light carbon in the spring of 1891."

The commercial development of carborundum had not proceeded far before Acheson brought out his process for the electric furnace production of artificial graphite and another great Niagara industry was founded. In quick succession came the Willson process for calcium carbide and the industrial applications of acetylene; phosphorus; ferro-alloys made in the electric furnace; metallic sodium, chlorine and caustic soda first by the Castner process, later by the extraordinarily efficient Townsend cell; electrolytic chlorates and alundum.

Perhaps even more significant than any of these great industrial successes was the Lovejoy & Bradley plant for the fixation of atmospheric nitrogen which was perforce abandoned. It is well to recall, in view of that reputed failure, that the present-day processes for fixing nitrogen have made little if any improvement in yields of fixed nitrogen per kilowatt hour over those obtained in this pioneer Niagara plant.

In the year 1800, a young assistant of Lavoisier, E. I. du Pont by name, emigrated to this country with others of his family and settled on the banks of the Brandywine, near Wilmington, Delaware. He engaged in the manufacture of gunpowder. To-day the du Pont Company employs about 250 trained chemists. Its chemical department comprises three divisions: the field division for the study of problems which must be investigated outside the laboratory and which maintains upon its staff experts for each manufacturing activity, together with a force of chemists at each plant for routine laboratory work; *second*, the experimental station which comprises a group of laboratories for research work on the problems arising in connection with the manufacture of black and smokeless powder, and the investigation of problems or new processes originating outside the company; *third*, the Eastern Laboratory which confines itself to research concerned with high explosives; its equipment is housed in 76 buildings, the majority being of considerable size spread over 50 acres. Since no industrial research laboratory can be called successful which does not in due time pay its way, it is pleasant to record that the Eastern Laboratory is estimated to yield a profit to its company of \$1,000,000 a year. In addition to the generous salaries paid for the high-class service demanded by the company, conspicuous success in research is rewarded by bonus payments of stock.

In Acheson and Hall have been already named two recipients of the Perkin medal, the badge of knighthood in American industrial research. The distinguished and thoroughly representative juries which award the medal annually had previously bestowed it upon Herreshoff for his work in electrolytic copper refining, the contact process for sulfuric acid and the invention of his well-known roasting furnace, and upon Behr for creative industrial research in the great glucose industry. In 1912, it was received by Frasch, and this year it was awarded Gayley.

The Gayley invention of the dry air blast in the manufacture of iron involves a saving to the American people of from \$15,000,000 to \$29,000,000 annually. A modern furnace consumes about 40,000 cubic feet of air per minute. Each grain of moisture per cubic foot represents one gallon of water per hour for each 1000 cubic feet entering per minute. In the Pittsburgh district the moisture varies from 1.83 grains in February to 5.94 grains in June, and the water per hour entering a furnace varies accordingly from 73 to 237 gallons. In a month a furnace using natural air received 164,500 gallons of water, whereas with the dry blast it received only 25,524 gallons. A conservative statement according to Prof. Chandler is that the invention results in a 10 per cent increase in output and a 10 per cent saving in fuel.

Especially notable and picturesque among the triumphs of American industrial research is that by means of which Frasch gave to this country potential control of the sulfur industry of the world. There is in Calcasieu Parish, Louisiana, a great deposit of sulfur 1000 feet below the surface under a layer of quicksand 500 feet in thickness. An Austrian company, a French company and numerous American companies had tried in many ingenious ways to work this deposit, but had invariably failed. Misfortune and disaster to all connected with it had been the record of the deposit to the time when Frasch approached its problem in 1890. He conceived the idea of melting the sulfur in place by superheated water forced down a boring, and pumping the sulfur up through an inner tube. In his first trial he made use of twenty 150 H. P. boilers grouped around the well, and the titanic experiment was successful. The pumps are now discarded and the sulfur brought to the surface by compressed air. A single well produces about 450 tons a day, and their combined capacity exceeds the sulfur consumption of the world.

An equally notable solution of a technical problem which had long baffled other investigators is the Frasch process for refining the crude, sulfur-bearing, Canadian and Ohio oils. The essence of the invention consists in distilling the different products of the fractional distillation of the crude oil with metallic oxides, especially oxide of copper, by which the sulfur is completely removed while the oils distill over as odorless and sweet as if from the best Pennsylvania oil. The copper sulfide is roasted to regenerate the copper. The invention had immense pecuniary value. It sent the production of the Ohio fields to 90,000 barrels a

day and the price of crude Ohio oil from 14 cents a barrel to \$1.00.

Turning from these examples of individual achievement so strongly characteristic of the genius of our people in one aspect, let us again consider for a moment that other and even more significant phase of our industrial research, namely, that which involves the coördinated and long-continued effort of many chemists along related lines.

Chemistry in America is essentially republican and pragmatic. Most of us believe that the doctrine science for science's sake is as meaningless and mischievous as that of art for art's sake, or literature for literature's sake. These things were made for man, not for themselves, nor was man made for them. Most of us are beginning to realize that the major problems of applied chemistry are incomparably harder of solution than the problems of pure chemistry, and the attack, moreover, must often be carried to conclusion at close quarters under the stress and strain induced by time and money factors. Under these circumstances it should not excite surprise that a constantly rising proportion of our best research is carried on in the laboratories of our great industrial corporations, and nowhere more effectively than in the research laboratory of the General Electric Company under the guidance of your past president, Dr. Whitney. As to the laboratory method Dr. Whitney says in a personal letter: "We see a field where it seems as though experimental work ought to put us ahead. We believe that we need to get into the water to learn to swim, so we go in. We start back at the academic end as far as possible, and count on knowing what to do with what we find when we find it. Suppose that we surmise that, in general, combustible insulation material could be improved upon. We try to get some work started on an artificial mica. Maybe we try to synthesize it and soon come to a purely theoretical question; *e. g.*, is it possible to crystallize such stuff under pressure in equilibrium with water vapor corresponding to the composition of real mica? This may lead a long way and call in a lot of pure chemistry and physical chemistry. Usually we just keep at it, so that if you haven't seen it on the market we're probably at it yet."

In striking contrast to the secrecy maintained between individual workers in large German research laboratories, is the almost universal custom in America to encourage staff discussion. In the General Electric Laboratory, as in many others, the weekly seminars and constant helpful interchange of information has developed a staff unity and spirit which greatly increases the efficiency of the organization and raises that of the individual to a higher power.

Many evenings could profitably be spent in discussing the achievements of this laboratory. Their quality is well indicated by the new nitrogen tungsten lamp, with its $\frac{1}{2}$ watt per candle, which combines the great work of Dr. Coolidge on ductile tungsten with the studies of Langmuir and others of the staff on the particular glass and gas and metal which are brought together in this lamp.

Any attempt to adequately present the enormous volume of research work, much of which is of the highest grade, constantly in progress in the many scientific bureaus and special laboratories of the general government or even to indicate its actual extent and range, is of course utterly beyond the limits of my attainments or of your patience. The generous policy of the government toward research is unique in this, that the results are immediately made available to the whole people. Heavy as some of the government reports are, they cannot be expected to weigh more than the men who write them. Some, like the Geochemistry of F. W. Clarke, are of monumental character. A vast number are monographs embodying real and important contributions to scientific knowledge or industrial practice. Some, as would be expected, are little more than compilations or present the results of trivial or ill-considered research.

The United States is still essentially an agricultural country and agriculture is, in its ultimate terms, applied photo-chemistry. The value of our farm property is already over \$42,000,000,000, and each sunrise sees an added increment of millions. Even small advances in agricultural practice bring enormous monetary returns. The greatest problem before the country is that of developing rural life. While our people still crowd into already congested cities, some are beginning to realize that Long Acre Square is not a wholly satisfying substitute for Long Acre Farm, and to question whether the winding, fern-fringed country roads of Vermont may not be a better national asset than the Great White Way.

Chief, therefore, among the Government Departments, in the volume of industrial research is of course the Department of Agriculture, which includes within its organization ten great scientific bureaus, each inspired by an intense pragmatism and aggressively prosecuting research in its allotted field. The magnitude of these operations of the Department may be inferred from the fact that it spent for printing alone during the fiscal year just ended \$490,000. The activities of its army of agents literally cover the earth, and its annual expenditure runs to many millions. The Bureau of Soils, the Bureau of Plant Industry, the Bureau of Animal Industry and the Forest Service have to do with the very foundations of our national existence and prosperity, and their researches have added billions to the national wealth. The Bureau of Chemistry, through its relation to the enforcement of the Pure Food Law and the inspection of meats before interstate shipment, is as ubiquitous in its influence as the morning newspaper and touches the daily life of the people almost as closely. The consumer is by no means the only one benefitted by its activities. Manufacturers are protected from the unfair competition of less scrupulous producers. The progress of research is stimulated not only by investigations within the Bureau, but by their reaction upon the manufacturers of food products who are rapidly being brought to establish laboratories of their own. The food work of the Bureau is supplemented and extended by the laboratories of the state and city boards of health,

of which that of Massachusetts has been notable for productive research. Special laboratories within the Bureau carry its influence and investigations into other fields as in case of the Paper and Leather Laboratory.

The Office of Public Roads of the Department, mindful of the fact that less than ten per cent of the total road mileage of the country has ever been improved, maintains a large organization of engineers, chemists and other scientists to conduct investigations and compile data, the ultimate purpose of which is to secure efficiency and economy in the location, construction and maintenance of country roads, highways and bridges.

The research work of the Department of Agriculture is greatly augmented and given local application through the agency of 64 state agricultural experiment stations established for the scientific investigation of problems relating to agriculture. These stations are supported in part by Federal grants, as from the Hatch and Adams funds, and for the rest by state appropriations. Their present income exceeds \$3,000,000. All are well equipped; one of them, California, includes within its plant a superb estate of 5400 acres with buildings worth \$1,000,000.

The station work is organized upon a national basis but deals primarily with the problems of the individual states. The efficiency of their work is stimulated by the requirement of the Adams Fund that appropriation shall be confined to definite projects. The number of such projects during 1910 was 335 and during 1911, 290. The reduction in number in no way implies diminished activity, and is due to more careful selection and preparation, with elimination of trivial and merely demonstrational projects. While the work of the stations necessarily covers a wide range of subjects, many of which would not be regarded as chemical in nature, a notable proportion has to do directly with chemical projects. Only the briefest reference can be made to a few of these:

At Connecticut, Osborne's studies of proteins and their feeding values have developed differences as great in their assimilability as those existing between the different carbohydrates.

Kansas has a department for the study of problems in handling and milling grain with an experimental baking plant for testing the bread-making capacity of flours. The millers are actively cooperating.

Minnesota has a similar thoroughly modern baking and testing laboratory for studies in wheat and flour chemistry and technology.

Arizona finds that date ripening may be so hastened by spraying the immature fruit with acetic acid that choice varieties are caused to ripen in that region.

The Cornell Station has demonstrated that the growth of a legume with a non-legume gives the latter a greater protein content than when grown alone.

Wisconsin has established the significance of sulfur as a plant food; grain crops, for example, remove nearly as much sulfur as they do phosphoric acid, whereas the soil supply of sulfur is far less.

Vermont is studying the forcing of plants by means of carbonic acid gas.

Idaho has raised the protein content of wheat, by 50 per cent. Kentucky has developed a method for the detection of *Bacillus typhosus* in water, and North Dakota is conducting very extensive field tests on the durability of paints and oils.

These are of course mere surface references which hardly touch the real work of the stations. An enormous amount of research and routine work on fertilizers is constantly carried on by methods standardized by the Association of Official Agricultural Chemists. The theory of the action of fertilizers engages the effort of many research workers who find the problem far more complex than the old plant food theory assumed.

It may be said without fear of contradiction that through the combined efforts of the Department of Agriculture, the Experiment Stations, the Agricultural Colleges and our manufacturers of agricultural machinery there is devoted to American agriculture a far greater amount of scientific research and effort than is at the service of any other business in the world.

No other organic substance occurs in such abundance as wood, and few if any are more generally useful. About 150,000,000 tons of wood are still wasted annually in the United States. The Forest Products Laboratory which is maintained by the Forest Service in coöperation with the University of Wisconsin has for its purpose the development and promulgation of methods for securing a better utilization of the forest and its products, and its research work is directed to that end. The laboratory is splendidly equipped with apparatus of semi-commercial size for work in timber physics, timber tests, wood preservation, wood pulp and paper and wood distillation and chemistry.

In the United States Patent Office, Dr. Hall has developed a remarkably comprehensive index to chemical literature which now contains 1,250,000 cards and which is open to every worker. The Bureau of Fisheries devotes \$40,000 to a single study and the Geological Survey, \$100,000 to the investigation of the mineral resources of Alaska. It spent, in 1913, \$175,000 for engraving and printing alone. The superb Geophysical Laboratory of the Carnegie Institution of Washington is also constantly engaged in the most refined researches into the composition, properties and mode of genesis of the earth's crust. The Smithsonian Institution is honored throughout the world for the efficiency of its effort to increase and diffuse useful knowledge among men.

The Bureau of Mines of the Department of the Interior was established to conduct in behalf of the public welfare fundamental inquiries and investigations into the mining, metallurgical and mineral industries. Its appropriation for the current fiscal year is \$662,000, of which \$347,000 is to be devoted to technical research pertinent to the mining industry. The Bureau has revolutionized the use of explosives in mines. Over \$8,000,000 worth of coal is now bought on the specification and advice of the Bureau while more than 50 of the larger cities, a number of states, and many corporations have adopted the Bureau plan of purchase. Our own

Dr. Parsons, as chief mineral chemist of the Bureau, is carrying its researches into new and interesting fields.

Perhaps no better evidence could be adduced of the present range and volume of industrial research in America than the necessity, imposed upon the author of such a general survey as I am attempting, of condensing within a paragraph his reference to the Bureau of Standards of the Department of Commerce. Its purpose is the investigation and testing of standards and measuring instruments and the determination of physical constants and the properties of materials. To these objects it devotes about \$700,000 a year to such good effect that in equipment and in the high quality and output of its work it has in ten years taken rank with the foremost scientific institutions in the world for the promotion of industrial research and the development and standardization of the instruments, materials and methods therein employed. Its influence upon American research and industry is already profound and rapidly extending. The Bureau co-operates with foreign governments and institutions, and is constantly consulted by state and municipal officials, technical bodies, commissions and industrial laboratories as a court of highest appeal.

I cannot better conclude this cursory and fragmentary reference to governmental work in applied science than with the words of the distinguished Director of the Bureau of Standards:

"If there is one thing above all others for which the activities of our government during the past two or three decades will be marked it is its original work along scientific lines, and I venture to state that this work is just in its infancy."

In view of the evidence offered by Germany of the far-reaching benefits resulting from the close co-operation which there obtains between the university laboratory and the industrial plant, it must be admitted with regret that our own institutions of learning have, speaking generally, failed to seize or realize the great opportunity confronting them. They have, almost universally, neglected to provide adequate equipment for industrial research, and, what is more to be deplored since the first would otherwise quickly follow, have rarely acquired that close touch with industry essential for familiarity and appreciation of its immediate and pressing needs. There are happily some notable exceptions. Perhaps foremost among them stands the Massachusetts Institute of Technology with its superb engineering and testing equipment, its Research Laboratory of Applied Chemistry and the meritorious thesis work of its students in all departments. The Biological Department has been especially active and successful in extending its influence into industrial and sanitary fields, while unusual significance attaches to the motor vehicle studies just concluded and the more recently inaugurated special investigations in electricity, since both were initiated and supported by external interests. About two years ago the Institute brought vividly before the community the variety and extent of its wide-spread service to industry by holding a Congress of Technology, at which all of

the many papers presented recorded the achievements of Institute alumni.

The Colorado School of Mines, recognizing that \$100,000,000 a year is lost through inefficient methods of ore treatment, has recently equipped an experimental ore dressing and metallurgical plant in which problems of treatment applicable to ores of wide occurrence will be investigated. The Ohio State University has established an enviable reputation for its researches in fuel engineering. Cornell has been especially alive to the scientific needs of industrial practice, and a long experience with technical assistants enables me to say that I have found none better equipped to cope with the miscellaneous problems of industrial research than the graduates of Cornell. It may in fact be stated generally that the quality of advanced chemical training now afforded in this country is on a par with the best obtainable in Germany, and that home-trained American youth adapt themselves far more efficiently to the requirements and conditions of our industries than do all but the most exceptional German Doctors of Philosophy who find employment here.

Several of the great universities of the middle west, notably those of Wisconsin and Illinois, have placed themselves closely in touch with the industrial and other needs of their communities and are exerting a fundamental and growing influence upon affairs. In the east, Columbia has recently established a particularly well equipped laboratory for industrial chemistry and is broadening its work in this department.

The Universities of Kansas and of Pittsburgh are carrying forward an especially interesting experiment in the operation of Industrial Research Fellowships supported by the special interests directly concerned. These Fellowships endow workers for the attack of such diverse subjects as the chemistry of laundering, the chemistry of bread and baking, that of lime, cement and vegetable ivory, the extractive principles from the ductless glands of whales, the abatement of the smoke nuisance, the technology of glass, and many others. The results obtained are intended primarily for the benefit of the supporters of the individual Fellowships but may be published after three years. The holder of the fellowship receives a proportion of the financial benefits resulting from the research, and the scale of sums allotted has progressively risen from \$500 a year to \$2500 and even to \$5000. While some doubt may reasonably be expressed as to the possibility of close individual supervision of so many widely varying projects, the results obtained thus far seem entirely satisfactory to those behind the movement, which has further served to strongly emphasize the willingness of our manufacturers to subsidize research.

The present vitality and rate of progress in American industrial research is strikingly illustrated by its very recent development in special industries. It has been said that our best research is carried on in those laboratories which have one client, and that one themselves.

Twenty-five years ago the number of industrial concerns employing even a single chemist was very small, and even he was usually engaged almost wholly upon routine work. Many concerns engaged in busi-

ness of a distinctly chemical nature had no chemist at all, and such a thing as industrial research in any proper sense hardly came within the field of vision of our manufacturers. Many of them have not yet emerged from the penumbra of that eclipse and our industrial foremen as a class are still within the deeper shadow. Meantime, however, research has firmly established itself among the foundation stones of our industrial system, and the question is no longer "What will become of the chemists?" It is now, "What will become of the manufacturers without them?"

In the United States to-day, the microscope is in daily use in the examination of metals and alloys in more than 200 laboratories of large industrial concerns.

An indeterminate but very great amount of segregated research is constantly carried forward in small laboratories which are either an element in some industrial organization or under individual control. An excellent example of the quality of work to be credited to the former is found in the development of cellulose acetate by Mork in the laboratory of the Chemical Products Company, while a classic instance of what may be accomplished by an aggressive individualism plus genius in research is familiar to most of you through the myriad and protean applications of Bakelite. The rapidity of the reduction to practice of Baekeland's research results is the more amazing when one considers that the distances to be traveled between the laboratory and the plant are often, in case of new processes and products, of almost astronomical dimensions.

Reference has already been made to the highly organized, munificently equipped and splendidly manned laboratories of the du Pont Company, the General Electric Company, and the Eastman Kodak Company. There are in the country at least fifty other notable laboratories engaged in industrial research in special industries. The expenditure of several of them is over \$300,000 each a year; the United States Steel Corporation has not hesitated to spend that amount upon a single research; the expenses of a dozen or more probably exceed \$100,000 annually. The limits of any address delivered outside a jail unfortunately preclude more than the merest reference to a very few. One of the finest iron research laboratories in the world is that of the American Rolling Mills Co. Equally deserving mention from one aspect or another are the laboratories of the Fire Underwriters, the National Carbon Co., the Solvay Process Co., the General Bakelite Co., Parke, Davis & Co., the Berlin Mills Co., the United Gas Improvement Co., the National Electric Lamp Association, Swift & Co., the Pennsylvania Railroad, and many others.

Research in the textile industries has been greatly stimulated by the various textile schools throughout the country, of which the Lowell Textile School with its superb equipment is perhaps best known. The fermentation industries have been brought upon a scientific basis largely through the efforts of the Wahl-Henius Institute at Chicago and other special schools. In the paper industry, general research is mainly confined to the Forest Products Laboratory at Madison,

its branch laboratory for wood pulp at Wausau, the Bureau of Standards, the Paper and Leather Laboratory of the Agricultural Department, and the laboratory of Arthur D. Little, Inc., at Boston. Our own special equipment for this purpose includes, as does that of some of the other laboratories named, a complete model paper mill of semi-commercial size.

There is no school of paper-making in the country, and one of our most urgent industrial needs is the establishment of special schools in this and other industries for the adequate training of foremen who shall possess a sufficient knowledge of fundamental scientific principles and method to appreciate the helpfulness of technical research. The Pratt Institute at Brooklyn is fully alive to this demand and has shaped its courses admirably to meet it.

The steel industry in its many ramifications promotes an immense amount of research ranging from the most refined studies in metallography to experimentation upon the gigantic scale required for the development of the Gayley dry blast; the Whiting process for slag cement; or the South Chicago electric furnace. This furnace has probably operated upon a greater variety of products than any other electric furnace in the world. Regarding the steel for rails produced therein, it is gratifying to note that after two and one-half years or more no reports of breakage have been received from the 5600 tons of standard rails made from its output. The significance of this statement will be better appreciated when we consider that in 1885 the average total weight on drivers was 69,000 lbs. It had risen to over 180,000 lbs. in 1907, and reached a maximum of 316,000 lbs. in that year. The weight of rails during the same period had increased from 65-75 lbs. to 85-100 lbs. In 1905, conditions were so bad that out of a lot of 10,000 tons, 22 per cent were removed the first year because of depressions in the head. In 1900, the American Railway Engineering Association took the matter in hand and studied the influence and extent of segregation of specific impurities. The work was at first confined to phosphorus but has been extended to other constituents. Fay called attention to the highly deleterious influence of sulfide of manganese.

The great railway systems have been quick to coöperate in these researches which with others of fundamental importance have been extended by the American Society for Testing Materials, the Master Car Builders' Association, and other organizations. Materials of construction have constituted a fertile subject of inquiry in the Structural Materials Testing Laboratory of the United States Geological Survey.

There could well be a further great enlargement of the field of industrial research in special industries through the initiative and support of National trade associations, to the great benefit of their membership. The American Paper and Pulp Association, for example, should subsidize studies in the utilization of waste sulfite liquors, the paper-making qualities of unused woods and fibers, the hydration of cellulose, new methods of beating the yields from rags, the proper use of alum and so on. The American Brass Founders'

Association could not do better than initiate investigations into zinc losses, the physical properties of alloys, and the production of alloys to specifications defining the properties desired, the application of the electric furnace to the industry and the preparation of new alloys by electric or other methods. A similar opportunity knocks at the door of the American Foundrymen's Association. Some few associations like those of the Bakers and the Laundrymen are already active to good purpose; others like the Yellow Pine Lumber Manufacturers' Association are aroused, but to the great majority of those powerful organizations, research is still an academic question to be discussed by their members individually if they so choose. Every industry has, however, its broad research problems, and its points especially vulnerable to research attack, among which it should be easy to select those of general interest to the industry as a whole.

There are in the country many analytical, testing and commercial laboratories, and, in most of these, special researches are conducted for clients, often with gratifying results. It is to be regretted, however, that there is not a more general appreciation among commercial chemists of the scale and quality of equipment and organization essential for really effective industrial research. As this broader viewpoint is attained, and the engineer's habit of mind acquired, we may expect a great extension of independent research, and the cessation of complaint regarding the trend of prices for analysis.

Among the relatively few private or incorporated laboratories with highly organized staff, and adequate special equipment, should be mentioned those of the Institute of Industrial Research at Washington, which has done notable work on the corrosion of metals, paint technology, canning, road material, cement, and special mill problems; the electrochemical laboratories of FitzGerald and Bennie at Niagara Falls, which have so successfully specialized on the construction and operation of electric furnaces to meet the requirements of special processes and products; the ore sampling and treating plant of Ricketts and Banks; and the Pittsburgh Testing Laboratory.

Industrial research is applied idealism: it expects rebuffs, it learns from every stumble and turns the stumbling block into a stepping stone. It knows that it must pay its way. It contends that theory springs from practice. It trusts the scientific imagination knowing it to be simply logic in flight. It believes with F. P. Fish, that, "during the next generation—the next two generations there is going to be a development in chemistry which will far surpass in its importance and value to the human race, that of electricity in the last few years. A development which is going to revolutionize methods of manufacture, and more than that is going to revolutionize methods of agriculture," and it believes with Sir William Ramsay that "The country which is in advance in chemistry will also be foremost in wealth and general prosperity."

With these articles of faith established in our thought, let us consider where they lead us. Within the last few days Frank A. Vanderlip, than whom no one speaks

with more authority upon financial matters, has told the assembled representatives of the electrical industries that they are facing a capital requirement of \$8,000,000 a week for the next five years—a total within that period of \$2,000,000,000. As chemists, we are ourselves entering upon an era in which the capital demands of industries now embryonic or not yet conceived, will in the not distant future be equally insistent and even more insatiable. Have we as chemists given a thought to this aspect of the development of our science, or planted the seeds of the organization which may some day cope with it? In the electrical and other established engineering professions, it is significant that the great industrial applications of the sciences involved have been in large part due to the activities of firms and organizations like Stone and Webster, J. G. White & Co., Blackwell, Viehle & Buck, and the United Gas Improvement Co., which, by an orderly but inexorable evolution, passed from the status of engineers to that of engineers and bankers. Our own profession has not yet evolved the chemist and banker, but such an evolution, or at least the close alliance of chemistry and banking is a fundamental prerequisite if the results of industrial research are to find their full fruition in America. Let me add that no field within the purview of the banker is more ripe for tillage or capable of yielding a richer harvest.

We need, however, to lead the banker to the chemical point of view, and even more do we ourselves require to be taught the financial principles involved in the broad application of chemistry to industry. To the ideals of service which inspire our profession, and which are so finely exemplified in Cottrell and made effective in the Research Corporation, we should add a stronger impulse to direct personal initiative in affairs. We shall need for years to prosecute a vigorous campaign for a better understanding by the general public of what chemistry is and what research is. The popular imagination is ready to accept any marvel which claims the laboratory as its birthplace, but the man in the works still disbelieves that two and two in chemical nomenclature make four. We need a multiplication of research laboratories in special industries, each with an adequate staff of the best men obtainable and an equipment which gives full range to their abilities. In nearly every case this equipment should include apparatus of semi-commercial size in which to reduce to practice the laboratory findings. Nothing is more demoralizing to an industrial organization, and few things are more expensive, than full-scale experimentation in the plant.

These laboratories should each be developed around a special library, the business of which should be to collect, compile and classify in a way to make all instantly available, every scrap of information bearing upon the materials, methods, products and requirements of the industry concerned. Modern progress can no longer depend upon accidental discoveries. Each advance in industrial science must be studied, organized and fought like a military campaign. Or, to change the figure, in the early days of our science, chemists patrolled the shores of the great ocean of the

unknown, and seizing upon such fragments of truth as drifted in within their reach, turned them to the enrichment of the intellectual and material life of the community. Later they ventured timidly to launch the frail and often leaky canoe of hypothesis and

returned with richer treasures. Today, confident and resourceful, as the result of many argosies, and having learned to read the stars, organized, equipped, they set sail boldly on a chartered sea in staunch ships with tiering canvas bound for new El Dorados.

ORIGINAL PAPERS

DESIGN OF SURFACE COMBUSTION APPLIANCES

By CHARLES EDWARD LUCKE¹

Received September 10, 1913

Manufactured gaseous fuel is and always will be more costly per unit of heat carried than natural fuel, and yet may yield cheaper and better service; cheaper if the process and apparatus used for the combustion of the gas is efficient enough, and better if it is so designed as to liberate the heat in a sufficiently more available form. It is this fact that justifies the general interest now shown in the process that has been termed Surface Combustion, which promises both cheaper and better gas service, the realization of which depends on the accumulation of much new data for the design of apparatus of commercial form. Some of this information has been worked out, and commercial apparatus of one or two classes designed therefrom. The process of development that has resulted in the establishment of surface combustion on an engineering basis whereby apparatus can now be designed to meet specific conditions is reported briefly in this paper.

ASSUMPTIONS OF NEW PROCESS

The new process assumes that gas to be burned should be supplied with no more air than will furnish the required amount of oxygen for the combustion reaction, and that the air and gas should be thoroughly mixed previous to combustion, so that the reaction may take place instantly, once the ignition temperature is reached. Excess air is regarded as not only useless but harmful because its heat absorption prevents the attainment of the highest temperatures so desirable when the heat of combustion is to be communicated to other bodies, and carries away as flue heat, quantities that would otherwise be of use. Premixture is regarded as desirable because thereby each particle of fuel may be brought positively into intimate contact with its required oxygen before it is needed, instead of depending on the accidental dissipation of the products formed on the edge of a flame jet, before the central core of gas can secure air from a surrounding and supporting atmosphere. This premixture, in conjunction with suitable proportioning, prevents the escape of unburned fuel in any form. Thus, premixture of air and gas in combining proportions at once insures protection against two important sources of loss in combustion: (1) that due to excess air and (2) that due to incomplete combustion. As an incidental accompaniment, another advantage of no less importance follows, and that is development of the heat of combustion in a form more available for absorption by the bodies to be heated, and

for the heating of which the gas is burned. Heat will be absorbed most readily from a fire when the temperature of the gases leaving the first is highest and when the fire zone is most radiant. All heat absorbed from the fire by direct contact of the absorber with the hot gaseous products is absorbed at a rate directly proportional to the excess of the temperature of the gases over that of the absorber; hence, the hotter these gases the more heat will a given absorbing surface take up, other things being equal. Heat is, however, much more rapidly absorbed by bodies when the source is radiant, because radiant heat readily pierces the insulating dead gas films adhering to the surface of the absorber and resisting by its low thermal conductivity all transmission from passing hot gas streams. The superior transmitting value of radiant heat has been well known as long as physicists have studied the sun's rays, but it has been lacking in most, though not all, gas burners because of the very low radiant value of hot gases as compared with solid bodies at the same temperature. The premixture of the gas and its supporting air makes it very easy to secure a large amount of the heat of combustion in a radiant form, because the combustion, being entirely independent of any atmosphere into which the products may be discharged, can be carried on behind layers of solid granules, in the crevices between them, in holes in solid plates, or behind solid plates of any convenient form, all of which, attaining the temperature of the gaseous products of combustion, radiate heat at a rate immensely superior to that of the gases themselves.

With all these prospective advantages in the direction of superior efficiency of this gas burning apparatus over all other modes of supply, the question naturally arises as to why the principles involved have not been more commonly practiced, and why there should be any delay in at once proceeding to the design of suitable appliances. The answer is to be found in the peculiar physical properties possessed by the gas and air over those now commonly in use, which make them difficult to control in the absence of detailed knowledge of their characteristics. In fact, without such knowledge, design of apparatus is quite impossible and it becomes feasible just in proportion as information of the needed sort is established by experimental research.

REQUIREMENTS OF PROCESS

The fundamental peculiarity of such mixtures is the property of self-propagation of flame through them, bringing them into the class of things commonly termed explosive. As all the mixture is in a condition suitable for combustion once the ignition temperature

¹ Professor of Mechanical Engineering, Columbia University, New York City.

is reached, it naturally follows that as the combustion temperature is much in excess of that of ignition, the burning of however minute a quantity of mixture at a point of ignition will promptly heat neighboring layers of mixture far above their ignition temperature so that the flame will, of itself, proceed through the whole mixture mass if it be isolated in a chamber. The only way such a self-propagation can be stopped is by preventing the heating of a fresh layer by the combustion of its neighbor, such prevention taking the form of a heat absorption by some solid screen at a rate great enough to permit the screen to take up the heat of combustion of all mixture in contact with one side without itself becoming hot enough to warm the mixture on its other side to the ignition point. It is easy to make such flame interrupting screens that will stop the propagation of flame through an explosive mixture once or twice, but difficult or impracticable to make them so as to be able to continue to do so indefinitely. With the exception of the internal combustion gas engine, gas burning apparatus requires a continuous burning of gas as supplied in a definite place termed the burner or furnace. When explosive gaseous mixtures are supplied to such continuous fires, the property of self-propagation operates to defeat localization of the combustion unless specific means are provided in the design of the structure to make the treatment of the mixture conform to its physical properties, in which case the combustion can be more definitely localized than otherwise.

For any given mixture there is a definite normal rate of propagation which may be equal to, less or greater than the velocity of flow of the mixture into the fire, and it is clear that localization of combustion will depend primarily on the relation of these two rates, that of flame propagation and that of flow. If they are equal, that is, if the flame can burn back toward the source of mixture supply, just as fast as, but no faster than the mixture reaches the flame, then will the flame remain fixed or be definitely localized. In fact, the above is the primary condition for localization of the combustion of explosive mixtures, because otherwise the flame would travel back to the source of supply or be blown out by the physical pushing away of the faster flowing fresh stream of mixture. Of course, localization may also be secured if the mixture will be fed through a flame-interrupting partition at a flow rate inferior to that of propagation, in which case the localization takes place on the face of the partition, which must, of course, have a large capacity for heat absorption indefinitely, *i. e.*, it must be able to dissipate or transmit to some other body the amount of heat it is receiving—otherwise it would rise in temperature to the point where it, by igniting the mixture on the supply side, would cease to be an interrupter.

Mixtures of the sort that seem best from the standpoint of efficiency of apparatus, having this explosive property, require a special treatment to permit of their use in commercial apparatus, which special treatment has for its first object the definite localization of the flame. The means employed must, moreover, be so positive as to be unaffected by long-continued operation;

that is, the localization must be permanent. There are, however, still other conditions to be met, such as control of rate of combustion per sq. ft. of fire or per cu. ft. of furnace, a cook stove requiring a low and a crucible furnace a high rate, and as such mixtures have what might be called a natural rate corresponding to the normal rate of propagation, it is clear that specific means must be available for burning slower or faster per sq. ft. of gas stream cross section. Furthermore, any one burner or furnace designed for some definite or normal rate of combustion or gas consumption, would be valueless commercially unless it would operate quite as positively at a wide range of variation, both above and below that normal rate. In other words, localization of the flame must not only be positive, and any desired rate of combustion be attainable by design, but in addition—hand or automatic interference with the designed rate of consumption must not in any way interfere with the localization.

In some cases it is desirable that the burner be capable of reaching its normal or steady working state in a short time, *e. g.*, in a domestic cook stove burner, while on the other hand a slow heating corresponding to a large heat storage in the furnace is necessary when articles are constantly being thrust in to be heated and then drawn out, without too much change of temperature in the furnace: hence, control of heat capacity of the burner must be available. Finally, there must be provided mechanical means for making the desired mixtures and for maintaining the desired proportions sufficiently, means so simple and automatic to require no more skill or attention on the part of the operator than appliances now in use.

Accordingly, this review of the work of development of the first commercial surface combustion appliances is divided into the following divisions:

I. Localization of Combustion Zone: *initially* on starting cold apparatus and *permanently* on attainment of the steady state of the fire.

II. Rate of Combustion per sq. ft. of Bed or Hearth for High Rates and Low.

III. Control and Adjustment of Radiating Surface.

IV. Auxiliary Apparatus.

V. Efficiency of Surface Combustion Appliances.

The experimental work here reported has all been done by or under the direction of the writer, partly in his laboratory at Columbia University, but largely in the laboratory of the Gas and Oil Combustion Co. in the Chemists' Building. Acknowledgment is freely made of the contributions of the laboratory staff, headed by Mr. Frank Creelman and including Messrs. E. J. Allen, H. L. Ocumpaugh, F. A. Wegener, W. B. Edison and Prof. E. J. Hall of Columbia University.

Only the results of N. Y. City illuminating gas are here reported, though work has been done with other fuels and satisfactory results obtained that permit the statement that all fuels in the gaseous or liquid form are equally available for the process.

I. LOCALIZATION OF COMBUSTION ZONE

Reasoning from the fact that the flame cap or surface over which combustion is proceeding will be steady in

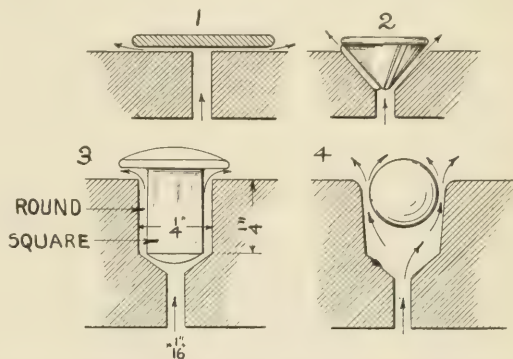
location only when the velocity of the mixture approaching it is equal to the rate of flame propagation for such a mixture, the first step in the design of practicable apparatus is the formation of gas passages of suitably changing area, since the velocity of gas flow for small changes of pressure will vary inversely as the cross section of the flow path. The mixture should approach the fire zone through a small tube or orifice at a rate greater than the normal velocity of flame, but immediately beyond there should be an enlargement of the cross section of the passage to permit of velocity reduction which, if carried far enough, would finally cause flow velocity to drop to equality with flame velocity, which was at the point of entrance in excess. Mechanical construction that will permit of this can be designed in almost endless variety, many of them equally good, but for the best results certain precautions must be observed: notably (1) the tendency for a gas jet escaping from an orifice under pressure to resist sidewise expansion so that even if the passage offers an increasing area for flow, the gas stream may not fill it unless forced to do so by baffles or their equivalent; and (2) the tendency for free jets flowing through a gaseous atmosphere of, for example, products of combustion, to entrain or diffuse with the atmosphere at the edges, becoming so dilute as to not burn properly, if at all.

GAS PASSAGES

Perhaps the simplest apparatus would be a very narrow angle conical passage to which mixture is fed at the smaller end; the stream expanding sidewise to always fill the cone would reduce in velocity and permit the location of a combustion surface quite definitely. In time such a conical tube would get hot; in fact, at the section where the flame surface located, it would become incandescent almost immediately if of refractory material, or melt off if of metal, and, of course, the narrower section along which the fresh mixture approaches would heat by conduction and warm the feeding gas. This mixture heating would tend to increase flow velocity and push away the flame surface if another counter influence did not prevent it; *i. e.*, the increase of flame propagation rate, which is due partly to rise of mixture temperature and partly to the accelerating effect of the hot solid walls. This counter influence accelerating combustion and drawing the flame surface back against the supply current is really stronger than the pushing away effect of velocity increase due to expansion of the stream by heating. Such cones are not in most cases good forms for the purpose because of the limit imposed on adjustment of rate of supply which if varied very much would cause a blow off or back flash of the flame, unless they were extremely long. When, however, a steady-rate apparatus is needed and flow is fixed, there may be just enough sidewise expansion of the jet issuing from a mere hole in a plate to locate the flame, but the practical uses of such apparatus are very small.

To meet the needs of every-day service there must be a more positive localization of the combustion surface, insensible to variation of mixture pressure or flow rate over a wide, though definite service range;

this requires specific provision for stream baffling so that the gas stream will increase in cross section rapidly beyond the supply point of minimum area and safe maximum flow velocity. Perhaps the simplest of these flame spreaders is a plate over the hole through which the mixture escapes as in Fig. 1. By placing



FIGS. 1 TO 4 MEANS FOR VELOCITY REDUCTION TO CONTROL LOCALIZATION OF COMBUSTION SURFACE

the baffle away from the plate carrying the orifice, a distance equal to one-quarter of the diameter of the orifice, the stream direction will be turned through a right angle without changing the flow velocity until the stream moves out under the plate beyond the hole, when, of course, the velocity will be reduced inversely as the diameter of the circle the gas occupies at any one time. With a hole $\frac{1}{16}$ of an inch in diameter a plate spaced $\frac{1}{64}$ of an inch away could reduce flow velocity when cold to $\frac{1}{8}$ of its entrance value if the plate were $\frac{1}{2}$ inch in diameter. This would permit an eightfold change in the rate of flow when cold, keep the flame surface always under the plate and give to the flame surface the form of a short cylinder. Such a construction offers some difficulties as in operation both plate and hearth would get very hot and unequally so; starting at the center the plate would remain dark, becoming incandescent from the flame zone out to the edge, which would crack most plates refractory enough to resist fusion even if a practical way of making such plates and holding them in position were available.

An easier construction is shown in Fig. 2, in which a solid (alundum cement) cone with three small ribs is placed in a counterbore of the feed hole. This is self-locating when in the position shown but not otherwise. Still another form that holds the baffle definitely against side movement is shown in Fig. 3, in which the baffle is shaped somewhat like a mushroom with a square-section stem fitting loosely in an enlargement of the feed hole so that the flow area does not change materially until the escaping mixture strikes the underside of the head and is deflected outward. The dimensions given are those used on some that gave good service with mixture pressures up to three inches of water though a little troublesome to make and apt to break if not gently handled. The most permanent form of this class of molded baffles is the refractory ball in a conical hole as shown in Fig. 4 and it is interesting to note that the ball, remaining suspended in

the jet and keeping, by reason of its weight, a constant velocity of the jet around it, insures the location of the flame above it, keeping it cooler than otherwise, so that fire clay balls have remained uninjured when the same clay a short distance above readily fuses. The physical action is here slightly different than in the previous cases, the escaping mixture forming an expanding and velocity reducing jet of ring form between the ball and its seat.

While, in the construction shown as typical, localization of the combustion surface is definite and mixtures may be burned in combining proportions, all fail to produce the uniform incandescence that is easily obtainable otherwise with such mixtures, though, of course, a series of such baffles spaced uniformly, approach this result; instead of a uniform glow they have a spotty appearance from black to truly incandescent. It is found, however, that any sort of porous screen placed in the path of the escaping gases will get uniformly hot. Such screens have been used of three sorts: (1) A perforated plate of metal, made of one of the non-oxidizable alloys such as are used in electric heaters. (2) A layer of granulated refractory material, the most satisfactory of which were made of Norton alundum. Of course, the less mass given to the screen the more rapidly it reaches incandescence initially and in this respect the metal screen is best; one of these placed $\frac{3}{8}$ inch over a hearth $4\frac{1}{2}$ inches diameter supplied with 55 holes each $\frac{1}{16}$ inch diameter and $\frac{1}{4}$ inch ball baffles heated in six seconds, while diaphragms thick enough to be mechanically strong may take five minutes, though, of course, the latter are more permanent. With the same arrangements except that the mushroom baffles were used instead, the following consumptions of gas were measured at the corresponding pressures and gave a steady dull red at the lowest rate and correspondingly brighter heats at the higher rates: 7.25, 9.1, 10.9, 12.2, and 14.2 cu. ft. of gas per hour at 1.00, 1.5, 2.0, 2.5 and 3.0 inches of water pressure. A similar set of mushroom baffles placed in a vertical hearth and having a screen of crushed fused silica $\frac{5}{8}$ inch deep of size between $\frac{20}{64}$ inch and $\frac{13}{64}$ inch, held in place by a second screen of wire mesh, heated to incandescence in $3\frac{1}{2}$ minutes at a supply pressure of 2 inches of water.

All the previously described baffling means intended to assist the spreading of the mixture stream beyond the point of high velocity supply, and many others of the same class, are used to counteract the natural tendency of gas jets to remain intact and resist side-wise expansion. It is possible, however, to make use of this natural tendency of jets and incidentally secure a very high degree of incandescence, higher in fact than is possible by any other known means, using air and the same gas. Moving the nozzle away from the baffle and making the baffle porous (using for convenience in experimental work a pile of refractory granules), the top or impact surface may be shaped to conform to the natural mushroom of the jet as it strikes. For any degree of porosity and jet velocity or supply pressure there is a best distance and a corresponding

impact face shape, that permits all mixture striking whether at the center or edges to have just the right velocity, that of propagation, in contact with the material, so that combustion takes place in contact with the outer or radiating surface which then has the maximum possible temperature. It is essential that the impact face be porous so that the products may

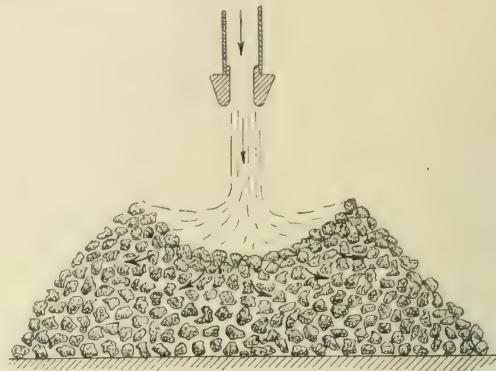


FIG. 5.—MEANS FOR LOCALIZING THE COMBUSTION ZONE AT THE EXTERNAL RADIATING SURFACE

readily escape through instead of forming dead gas films which separate the combustion surface from the solid faces and insulate the latter from the heat of the former. In this manner a surprising degree of radiance is obtained due to the high rate of combustion of a mixture containing no excess air except possibly at the outer edges by entrainment. At 3.2 inches mixture pressure, 40 cu. ft. of gas per hour were burned over about four square inches of surface, which corresponds to over 1400 cu. ft. per sq. ft. per hour and more than 800,000 B. T. U.'s per hour per sq. ft. Higher rates of combustion than this are obtainable but not all developed on the radiating surface itself.

PROPERTIES OF GRANULAR BEDS

In view of the importance of developing as large an amount of heat as possible in the radiant form, in addition to the localization of the combustion zone, and considering that loose granules or a porous diaphragm of refractory may serve the double purpose of the radiating screen and of the actual baffling or mixture stream spreader, everything else may be abandoned in favor of these refractories except perhaps for certain special purposes for which special forms may be best. Nearly all the work done has been concentrated on an effort to learn how these granular beds and bonded diaphragms should be handled to yield commercial apparatus, and by reason of the simplicity of the loose bed it has been consistently favored for most uses over the bonded.

A uniform grained bed of loose granular material will act as a substantially perfect spreader of the mixture issuing from an orifice covered by the bed but the quantitative effect of variations in size of grain, imperfections in shape or non-uniformity of size, together with shape of bed and its relation to shape, size and position of the feed orifice, are all to be de-

terminated by experiment only. Most of the detailed data of this sort will be omitted as not of general interest but the following series of experimental determinations illustrate the most important of the general principles that must be observed for successful operation: One of the simplest imaginable arrangements is shown in Fig. 6, where a single nozzle $\frac{5}{16}$

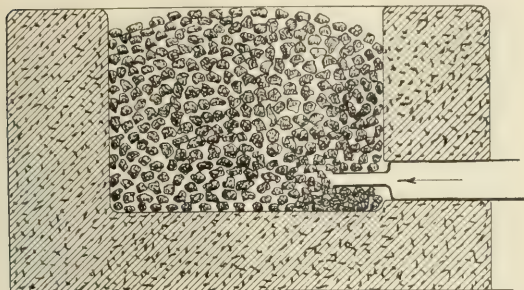


FIG. 6—APPARATUS FOR DEMONSTRATING THE SPHERICAL FORM OF THE COMBUSTION SURFACE WHEN MIXTURE IS SUPPLIED FROM A NOZZLE SURROUNDED BY GRANULAR REFRACTORY

inch in diameter projects $1\frac{1}{4}$ inches into a bed of broken fire brick which material is very convenient for studying the ultimate position and shape of the combustion zone as it will fuse and bond at that place. The bed was held in a square brick box $6\frac{3}{4}$ inches on a side and 5 inches deep and the nozzle was fed with mixture at 3.2 inches pressure. Starting with coarse grains $\frac{1}{2}$ inch to $\frac{3}{8}$ inch, the mixture on ignition flashed instantly down through the bed, locating below, quite near the nozzle as was shown later by the more or less spherical lump that fused there. The same action took place with smaller grain as it was reduced in size successively from $\frac{3}{8}$ inch to $\frac{5}{16}$ inch, $\frac{3}{16}$ inch to $\frac{1}{4}$ inch, $\frac{1}{4}$ inch to $\frac{3}{64}$ inch, $\frac{3}{64}$ inch to $\frac{5}{32}$ inch and $\frac{5}{32}$ inch to $\frac{3}{32}$ inch, but a further reduction in size resulted in a different action. On using grains from $\frac{3}{32}$ inch to $\frac{1}{16}$ inch in size, the mixture on ignition burned on top instead of flashing down through the voids to its normal surface about the nozzle. In a few minutes the top layer became hot and then seemed to cool; but on scraping away the top it could be seen that the combustion surface had receded; after running a sufficient time this progressive heating from the outside down toward the nozzle resulted in a final location of the combustion zone about where it was in the coarser material, in which it flashed back *instantly* to its normal position. Of course, in either case, the whole bed gets hot in time, but with coarse grains it heats from the normal combustion zone near the nozzle out and upward, while with small enough grain the outside top heats first, the flame drawing down slowly, a difference in action which requires an explanation.

When the grain is fine enough it acts like a flame interrupting screen, each little crevice between neighboring grains discharging so little mixture that its heat of combustion can for an appreciable time be absorbed by the solid grain in contact without raising the lower side to the ignition point, radiation from the outside surface helping to keep down the temperature.

In time, however, the lower side of the top layer gets hot and the combustion surface recedes, doing so more rapidly once it has passed under the top layer because then radiation cooling is lessened, leaving more heat for the grain to take up. It follows also that as with the finer grain less total mixture will escape from such a round nozzle as it tends to fill the orifice, so the total amount of heat developed will be less than with coarse grain. To show that the stoppage of the nozzle by the grain reducing the total gas flow and heat generation with fine grain is not responsible for the difference in flame action at the start as compared with coarse grain but that the difference is due to the difference in the mode of gas flow through the bed itself with corresponding more intimate contact be-

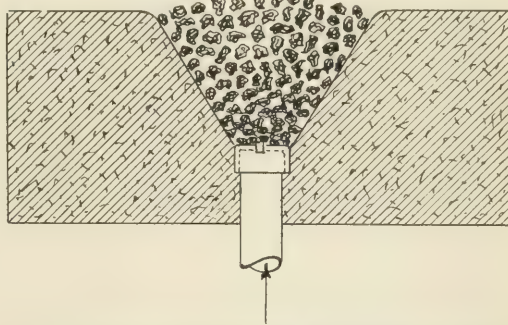


FIG. 7—APPARATUS FOR DEMONSTRATING UNIFORMITY OF POSITION OF COMBUSTION SURFACE WITH DIFFERENT SIZES OF GRAIN

tween mixture and grain the smaller the latter, the same series of results were obtained in a pyramidal chamber, shown in Fig. 7, in which the nozzle is a pair of hacksaw cuts in a 1-inch pipe cap, the whole being shown in the photo, Fig. 8. With such slot outlets for the mixture the flow is substantially the same for all the different sizes of grain given, yet not only did the top heat first with the $\frac{3}{32}$ inch to $\frac{1}{16}$ inch

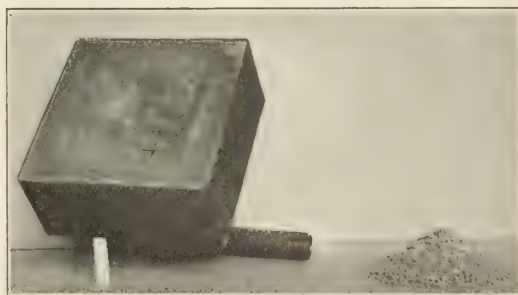


FIG. 8 APPARATUS FOR DEMONSTRATING UNIFORMITY OF POSITION OF COMBUSTION SURFACE WITH DIFFERENT SIZES OF GRAIN

grain and then burn back but also with the larger $\frac{5}{32}$ inch to $\frac{3}{32}$ inch with which it required ten minutes to draw the combustion zone down through the bed to its normal place and fuse a lump of granules over the cross slot.

In establishing the action just described the use of fire brick for the grain was most satisfactory as each

test gave a fixed record (in the form of a fused lump) of what had happened, but once it was clear that the size of grain made only a starting or temporary difference in action, then longer runs became desirable to bring out the possible heating effect on the nozzles; for these refractory grain was used, including magnesite, chrome ore, both natural lumps and broken brick, fused silica, lime and alundum. With these materials the long runs showed that some forms of feed orifices became heated so as to ignite the mixture in the feed pipe while with others this action did not take place, permitting operation for an indefinite time. It was not clear at the time just what caused the trouble since it frequently happened that the nozzle that worked best was really much hotter than another that flashed back almost as soon as the steady state was established. At any time an increase in the pressure at which the mixture was supplied would have so increased the volume of flow as to drive the combustion surface to a safe distance from the nozzle but it was deemed unwise to leave the matter here because, *first*, all domestic apparatus must operate on low pressure, lower than that of the gas in the local mains, and *second*, all industrial apparatus for which gas pressure boosting would not be objectionable would, at some time, be operated at part capacity or turned down, which is equivalent to low pressure operation.

PERMANENCE OF FLAME SURFACE

The next question investigated, therefore, was this permanence of the localization of the flame surface or combustion zone, and the discovery of means for securing an indefinite time of operation without disturbance from long-continued heating even over several days and with mixture pressures so low as to heat the hearth end of the nozzle above the ignition point. It is clear at the start that iron, or in fact any *metal*, must be kept away from the feed orifice proper, which in effect means that in order that appliances may operate on low pressures it is necessary that the mixture enter the fire chamber through a refractory orifice, or when the burner is lined with refractory, as it should be, the mixture must enter through a hole in the lining or what might be properly called the hearth. Using different mixture entrances a long series of experiments were made that were for a time extremely puzzling but which finally could be summed up in a very few words. All feed holes will become incandescent at the fire end with low gas pressures; heat will flow back through the bounding material of the hole and these hot walls will heat the mixture passing through. No harm will result, however, even from a bright red heat on the walls of the hole, provided the latter is of uniform bore over the heated part and has no enlargement of cross section with its corresponding low mixture flow velocity except at points that never get hotter than the point of ignition. To put it otherwise, the mixture passageway may be at any temperature without harm if of uniform bore and if when cold the flow velocity is great enough to prevent back flash. Under these conditions localization of the combustion will be permanent. Naturally anything that will reduce the tem-

perature of the supply tube, like radiation to the air, will also shorten the length of the necessary uniform bore portion as will also the use of more non-conducting material. Finally it was found that the length of uniform bore feed pipe that would be cool enough at its supply end to be joined to a larger mixture header or box, was greater for large than for small holes or that the allowable length was a definite number of diameters. For example, in an apparatus such as is illustrated in Fig. 9, with a single refractory lined tube

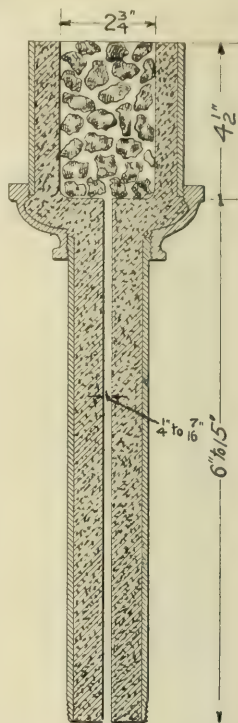


FIG. 9—APPARATUS FOR DETERMINING THE RATIO OF LENGTH TO DIAMETER OF FEED HOLE TO CONTROL "BACK HEATING"

feeding a cylindrical combustion chamber, all of alundum cement encased in metal, a hole of $1\frac{1}{4}$ inch diameter and 6 inches long could be operated indefinitely at 1 inch water pressure even after the chamber had been made very hot by previous operation at much higher pressures, whereas a $7\frac{1}{16}$ inch diameter hole of the same length flashed back at 1.5 inches water pressure, and continued to do so after periods ranging about three hours even after its length had been increased to 15 inches. Small diameter orifices of say $1\frac{1}{16}$ inch diameter have, on the other hand, been operated indefinitely on pressures as low as 0.2 inch of water when about $1\frac{1}{2}$ inches long. Back flash after long periods of operation by heating up of the supply system may, therefore, be prevented by proper design; i. e., by selection of suitable proportions in accordance with the announced principles and the established data, localization of the combustion zone will be correspondingly insured against disturbance.

II. RATE OF COMBUSTION PER SQ. FT. OF BED OR HEARTH

Passing now from the discussion of localization of the combustion zone or flame surface and the means for keeping it permanently localized, the next question of importance is that of control of rate of heat generation per sq. ft. of fire bed, which is a problem of distribution of the burning mixture over surfaces as large or small as may be demanded and of maintaining high or low degrees of incandescence over these surfaces. This now seems a very simple matter but for a considerable time it seemed even more elusive than the prevention of back flash through nozzles, which was annoying enough. There are really two problems here and though related, the relation is not as clear as it may seem. *First*, the problem of the high rate—At how high a rate may gas be burned and how may the

structure be formed so as to permit of steady supply and combustion at this rate over any given surface? *Second*, the problem of the low rate—Can such mixtures be burned so slowly as to keep a surface just hot enough for fusing for example; may such a burner be turned down to a so-called simmering point without giving trouble and if so, what ideas must be incorporated in the construction?

HIGH RATE OF COMBUSTION

The problem of the high rate is the simpler of the two, as this may properly be termed the natural rate, assuming, of course, that suitable refractories are obtainable for the corresponding high temperatures and that the principles of permanent localization of the combustion zone are understood and incorporated in simple constructions of apparatus. When the whole cross section of bed is taken up by the burning gas stream or when the combustion zone occupies the whole of the bed cross section, then mixture is being supplied as fast as it can be burned within the space available and any increase in rate of supply will tend to push the combustion zone away or result in the phenomenon of blow off. This is the condition at the limiting high rate of combustion and is the natural rate, because the advancing stream of mixture fills the whole available cross section of fire zone and combustion surface coincides with bed cross section in area. To establish this high rate it is necessary that at first when everything is cold, the mixture be supplied at a lower rate and then after the bed is heated, its accelerating effect may be relied upon to hold localized a very much increased rate of mixture supply up to a certain maximum, which is the natural or high rate of combustion. This natural high rate is intimately associated with the pressure of the mixture at the point of supply, or more properly, the drop in pressure through the feed holes or orifices, for holes of any given size. For example, in such a simple apparatus as that of Fig. 9, where a single feed hole supplies a combustion chamber of larger cross section, carrying a loose granular bed, it is evident that at some low pressure the combustion surface will just cap the feed hole and the rate of combustion will be natural for a bed area equal, not, to the actual bed of $2\frac{3}{4}$ inches diameter, but on the contrary, equal to that of the feed hole, a fraction of an inch in diameter. Increase of mixture supply pressure will push the combustion surface away from the hole until finally it will extend across the whole bed and have a form approximating a section of a spherical surface lying within a cylinder, the axis of which passes through the center of the sphere, which latter will be located at the center of the feed hole. It is this latter condition that gives the high rate and to secure it the supply pressure must be big enough to send through a small feed hole, say $\frac{1}{4}$ inch in diameter, enough mixture to spread out and fill the voids in the bed $2\frac{3}{4}$ inches in diameter, which will exceed half the free cross section, while at the same time the flow velocity through the enlarged cross section must be as great as the rate of flame travel backward. If the ratio of bed area (with a given percentage of voids) to feed hole area is large, then high mixture

pressures must be used to secure the natural high rate; so if only small mixture pressures are available then the free flow area of the bed may not exceed the area of the feed hole by very much. In any case large beds may be heated by the high rate of combustion, only by multiplication of orifices spaced at distances equal to the diameter of the combustion surface natural to the supply pressure in use. Before such spacing of feed holes for high natural rates of combustion can be found, it is first necessary to investigate the action for a single hole in a given bed, to find the relation between feed pressures and the ratio of active bed area to feed hole area that will cause the combustion surface to fill the whole bed between the enclosing walls. As an illustration of the method of procedure, it being impossible here to record much of this sort of data, the results of a single series on the apparatus shown in Fig. 9 will serve. In this series the pressures were never extended above 12 inches of water at the point of mixture supply and began with a single hole $\frac{5}{16}$ inch in diameter, discharging into a cylinder $2\frac{3}{4}$ inches in diameter, area 6 sq. inches, but as increase of pressure to the maximum noted failed to supply as much mixture as could be consumed in the available area, there was added a second, a third and finally a fourth hole, even then not reaching the limit.

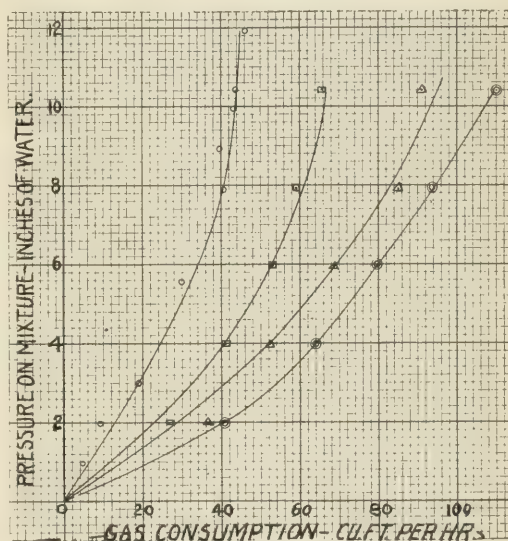


FIG. 10. RATE OF FLOW OF MIXTURE THROUGH DIFFERENT NUMBERS OF $\frac{5}{16}$ " FEED HOLES AT VARIOUS PRESSURES

With the four holes and at a pressure of $16\frac{1}{2}$ inches of water, there was attained a rate of combustion consumption of 2460 cu. ft. of gas per sq. ft. of bed per hour, which on a calorific value of 600 B. T. U. per cu. ft. is equivalent to 1,584,000 B. T. U. per hour per sq. ft. There was no indication that the limit had been reached, but as the rate was high enough for practical purposes and so high as to give trouble with available refractory materials, this series was not carried beyond these limits, though it could easily

have been done with high pressures or with a larger feed area than from $\frac{1}{16}$ inch hole ($= 0.3$ sq. in.). The conclusion here is, that rates higher than have been known are easily obtainable and rates higher than any refractory in common use can resist; hence, if any service arises that demands such rates, the need can be met. It might be noted here that of several refractories tried, the most satisfactory found was white alundum, with linings of alundum cement, preferably mixed with alundum grain of several sizes, properly proportioned dry to fill the voids, then mixed wet, rapidly dried and finally baked at a bright red heat. The size of grain in the loose bed and the depth of bed each exert an important influence within limits but in general for these high rates the larger the grain the better, though there is little, if any, advantage beyond one inch diameter, the depth in any case being little more than sufficient to prevent the gases lifting the grain off the hearth. The resistance in the bed is always appreciably less for round grain than for flat and in this respect the form of fracture of white alundum is most satisfactory. In the above mentioned series white alundum from $\frac{1}{2}$ inch to $\frac{3}{4}$ inch diameter was used and the depth averaged 2 inches. The results of this series are given in curve form, Fig. 10.

LOW RATE OF COMBUSTION

Probably the most difficult of these experimental problems was that of finding a suitable structure for the permanent localization of the combustion surface for very low supply pressures, while at the same time securing any desirably low rate of combustion over the bed with a uniform incandescence at the surface such as would be suitable for cooking, for example. It is clear that the lower the pressures the closer to the feed hole will the combustion surface locate, the smaller the area of bed heated, and the stronger the tendency to back flash. This fact led to early attempts to secure low rate heat distribution by other means than that of feed hole supply with a series of spots, each having natural high rates of combustion, located practically at the mouth of the holes. Mixture supplied to a passageway filled with fine granules or a porous brick, will flow much the same as through a pipe as the porosity supplies a multiplicity of small paths more or less mutually communicating, and a given quantity flowing would have a mean velocity through such a porous layer the same as through a pipe of cross section equal to the voids except for differences in friction. Mixture fed into such a fine bed in any convenient way, ranging from a single hole under a thick bed to a great number of holes under the whole bed obtainable by a metallic screen support for loose granules or the under surface itself of a bonded diaphragm, would discharge the mixture uniformly from the top of the bed, however the supply was arranged, if the bed were thick enough. This seemed to be at first the most promising idea to follow for low rate heat distribution especially as changes of area of flow path so necessary for localization can be obtained by two means quite conveniently: *first*, by using two layers with the upper coarser and, therefore, with more free voids than the lower fine bed; *second*, by changing

the diameter of the containing walls that hold the porous bed.

At first only loose granules were used in apparatus such as shown in Fig. 11, where a perforated metal plate of 306 holes per sq. in., diameter 0.033 inch, and 27.8 per cent free opening is supplied by a $\frac{3}{4}$ inch

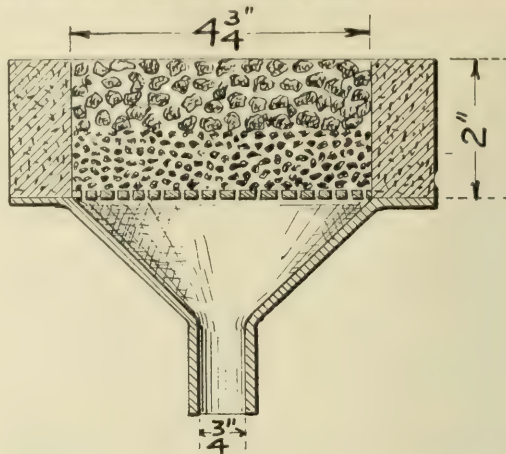


FIG. 11—MEANS OF CONTROLLING SURFACE DISTRIBUTION OF HEAT BY MIXTURE SUPPLY TO FINE GRANULAR BED ON THE SCREEN

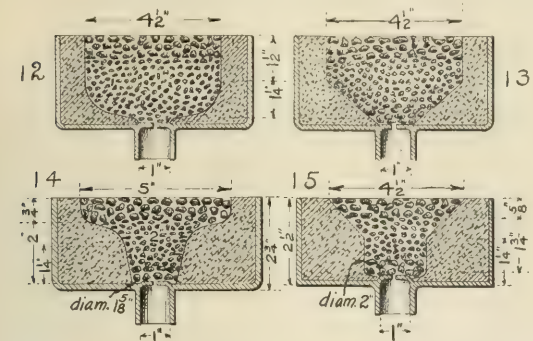
pipe, discharging into a conical space under the screen. On the top of the screen rests a one-inch bed of granules $\frac{8}{64}$ inch to $\frac{6}{64}$ inch and over it another one-inch layer of larger grain, $\frac{24}{64}$ inch to $\frac{20}{64}$ inch diameter. On lighting the mixture supplied at 2 inches water pressure the combustion zone instantly locates between the layers at the point of change of free flow space, due to the difference in voids, but as the heat penetrates the lower or fine bed, the combustion zone works back to the screen, which happens with these conditions in about ten minutes. All sorts of changes in the relative sizes of the material and thickness of the two beds or number of layers yield no difference in the result except as to the time it takes the combustion zone ultimately to work back to the screen, burning it out, causing a flash back, or both. This is clearly due to insufficient velocity of flow at the supply end of the bed and suggests a contraction of the walls toward the lower end, as in Fig. 12, where a slot supply is substituted for the screen as it does not burn out so readily if by accident the flame should work down that far. As before, however, the combustion zone worked down close to the nozzle but not so quickly as before, suggesting a further narrowing at the bottom to form a neck as in the forms successively tried, and shown in Figs. 13, 14 and 15. As the neck is thus narrowed the combustion surface no longer approaches the nozzle so closely, stopping, in Fig. 13, about 1 inch above after $\frac{3}{4}$ hour at $3\frac{1}{2}$ inches pressure, in Fig. 14 about $1\frac{1}{2}$ inches above, while in Fig. 15 it did not enter the lower cylindrical portion at all.

By adjusting the space between the walls, the flow velocity through the lower or fine bed can, therefore, be kept high enough to control the location of the combustion zone, regardless of the manner of feeding

the mixture to its narrow bottom part, but the problem is by no means solved. All these latter forms are bad

hole plate is out of the question unless provided with means for removing heat received on the combustion chamber face, fast enough to balance heat conduction through it toward the source of supply, and effective enough to prevent that side from becoming a point of ignition.

Since it has been shown that a single long feed hole supplying a combustion zone can be proportioned so as to permanently resist backward heat flow well enough to insure indefinite periods of operation, it naturally follows that several feed holes might be grouped so as to be fed from a common point, discharging mixture at the other end over as large an area as needed for any desired surface rate of combustion, and so proportioned as to resist heat flow as effectively as with one, if the necessity for the latter is kept clearly in mind. This conception is the basis of the construction shown in Fig. 16 which has 30 holes molded in alundum cement by wires held in hole plates at the end and radiating from a $1\frac{1}{2}$ -inch bottom chamber in the iron container casting, to a $4\frac{1}{4}$ -inch diameter circular top bed. To insure the supply chamber end of these feed holes against a rise of temperature to the ignition point, it is necessary only that the distance between



FIGS. 12 TO 15—APPARATUS FOR CONTROLLING POSITION OF COMBUSTION SURFACE FOR A GIVEN HEAT DISTRIBUTION OVER THE RADIATING SURFACE

in another respect because with the thickness of bed above the combustion zone the top is hot in the center and cool at the edges. To get an even top heat, a greater thickness of bed above the combustion zone would be required but this is already too thick to give a quick initial heating, so another change in construction is suggested, incorporating a different relative position of the narrow lower neck of fine material in the top surface maintaining about the same relative areas as in the last case, which were found sufficient to hold the combustion zone above the cylindrical portion. Such an alteration was made by enlarging the cylindrical portion and inserting a solid core $3\frac{1}{2}$ inches in diameter so the mixture rose in a thin ring $\frac{1}{4}$ inch thick around the core filled with fine material and then spread out at the top, heating a bed of 5 inches diameter. This gave a better top heat distribution but took too long to reach a steady state—almost an hour. After many trials of various proportions it became clear that if uniform top temperatures are to be quickly obtained with low rates of gas consumption over an extended surface that single feeds through single or double porous beds will not suffice and some other plan must be employed.

USE OF MULTIPLE FEED ORIFICES

The failure of the single point supply to distribute mixture so as not to flash back and yet quickly and uniformly heat the top of a radiating bed, with a low rate of combustion, leads to the conclusion that multiple feed orifices must be used, so spaced as to give the heat distribution desired at the available pressure, a surface bed or radiating screen of sufficient thickness serving to localize the combustion and to equalize the otherwise spotty appearance. It might appear that this could be done by drilling holes in a plate and dividing the combustion chamber from the mixture supply chamber, but from what has been said about the conditions for permanent localization of the combustion zone, it is clear that such an orifice plate will sooner or later heat through, becoming hot enough on the supply side to ignite the mixture there before its entrance into the feed holes. Any sort of feed

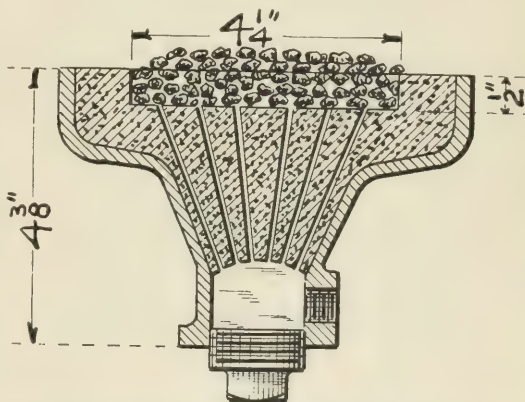


FIG. 16—FIRST COOK STOVE TOP BURNER IN WHICH LOCALIZATION OF COMBUSTION SURFACE, BACK HEATING, DISTRIBUTION OF HEAT OVER RADIATING SURFACE ARE ALL CONTROLLED

this point and the hearth be long enough. When it is, the dissipation of heat from the side walls will be large enough to balance the heat carried down through the solid material surrounding the holes, and the dimensions shown in the sketch have proved to be adequate for this purpose.

FIRST PRACTICAL STOVE BURNER

In Figs. 17 and 18 are shown two photographic views of the first reasonably practical burner for stove service operating on surface combustion principles—but still imperfect in some respects. To uniformly heat the top bed of loose grain of white alundum or broken fused silica, half an inch thick, thirty-four holes were molded, as shown, by wires $\frac{1}{16}$ inch in diameter and spaced in three rings. This arrangement gave a quite uniform top heat and was operative at low gas and mixture pressures for an indefinite time, for although the holes of the central group were often red hot for

over an inch below the hearth the heat dissipation from the sides was always sufficient to prevent the



FIGS. 17 AND 18—FIRST SUCCESSFUL COOK STOVE TOP BURNER, SOLID TYPE

lower end of the holes ever reaching the ignition temperature. The proportions used were selected to give consumption somewhere near those of the standard top burners of ordinary gas cook stoves, that is, at

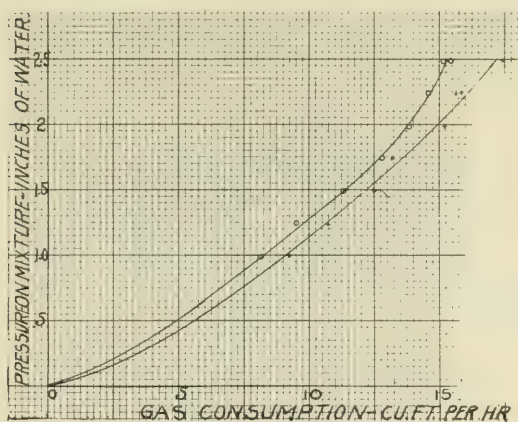


FIG. 19—RATE OF COMBUSTION AT VARIOUS PRESSURES ON CIRCULAR BED, $4\frac{1}{4}$ " IN DIAMETER, SUPPLIED BY 34 HOLES, EACH $\frac{1}{16}$ " IN DIAMETER. UPPER CURVE FOR A BED OF WHITE ALUNDUM, $20/64"-24/64"$ GRAIN, $\frac{1}{2}$ " THICK. LOWER CURVE FOR A BED OF FUSED SILICA $20/64"-24/64"$ GRAIN, $\frac{1}{2}$ " THICK

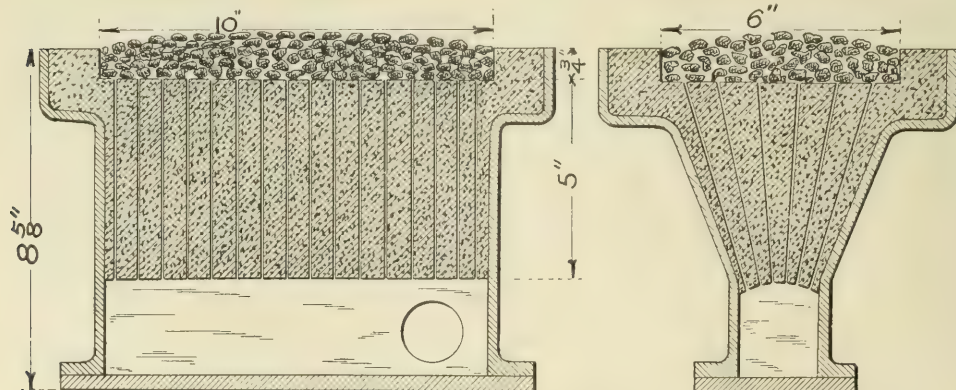


FIG. 20—FIRST FORM OF MUFFLE FURNACE BURNER, SOLID TYPE

which is equivalent to about 100 cu. ft. of mixture. Naturally, variations in bed thickness, size of grain or even kind of grain, will cause changes of resistance, the latter due to the variations in the voids, corresponding to different characteristic fractures. The characteristic consumption tests at various low pressures are given in curve form, Fig. 19, showing that at 2.5 inches water pressure this stove burner consumed about 17 and $15\frac{1}{2}$ cu. ft. of gas with the silica and white alundum beds, respectively, the standard of 15 cu. ft. per hour being equivalent to 150 cu. ft. per hour per sq. ft. By varying the diameter length and spacing of holes, keeping the general arrangement here indicated, practically any desired rate is obtainable though the general design is the result of the search for a construction suitable for a properly distributed low rate of combustion.

ADAPTATIONS OF TYPE BURNER

To illustrate the ease of adaptability of this general type construction of surface combustion burner to any desired rate over any surface, three other burners are shown, one each designed for a muffle furnace, a crucible furnace and a steam boiler fire, respectively.

The first of these, intended for placing below an assay muffle, is shown in sketch form in Fig. 20 and photographically in Figs. 21 and 22, on which latter the chalk line indicates the beginning of the feed holes. This burner had a rectangular hearth, 6 inches by 10 inches, supplied by 96 holes, molded in alundum cement in a cast iron casing and at 3 inches of water mixture pressure consumed 120 cu. ft. of gas per 60 sq. inches, equivalent to 288 cu. ft. per hour per sq. ft.

A still higher rate over an annular hearth was obtained in the small crucible furnace burner of the same general type as shown in Fig. 23, the combustion zone lying between the side insulation and a central cylindrical muffle used to keep the crucible chamber clear but not at all essential to the operation, though it helps to keep the crucible bottom cooler than it would be otherwise. In this burner 20 holes, each 0.14 inch in diameter, were distributed so as to be

mixture pressures of $2\frac{1}{2}$ inches water the consumption was intended to be about 15 cu. ft. of gas per hour,

on the surface of a cone supplying a hearth lying between two circles, $4\frac{1}{2}$ inches and $2\frac{3}{4}$ inches in di-

ameter, the area of which is, therefore, $15.9 - 5.9 = 10$ sq. in. The combustion was 40 and 47 cu. ft. per hour

tried out in the fire box of the Baldwin locomotive in the Mechanical Engineering Laboratory at Columbia University as to its capacity and the proper design

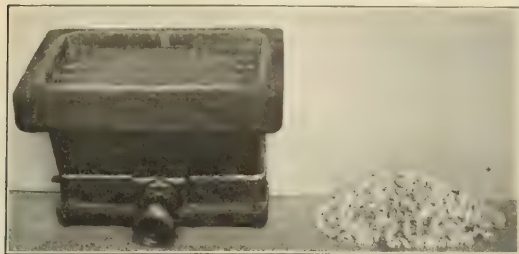


FIG. 21—TOP VIEW OF SOLID TYPE OF MUFFLE FURNACE BURNER AND WHITE ALUNDUM LOOSE GRANULAR BED

at 2.5 inches and 3.0 inches, respectively, which are equivalent to 576 and 677 cu. ft. per hour per sq. ft. of hearth.

An example of how this type construction may be

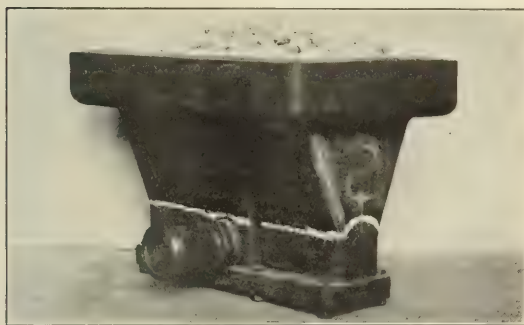


FIG. 22—SIDE VIEW OF SOLID TYPE MUFFLE FURNACE BURNER; BED IN PLACE

adapted to extension of hot surface or hearth over large areas without excessive length of holes in the solid group is shown in the photograph, Fig. 24, where

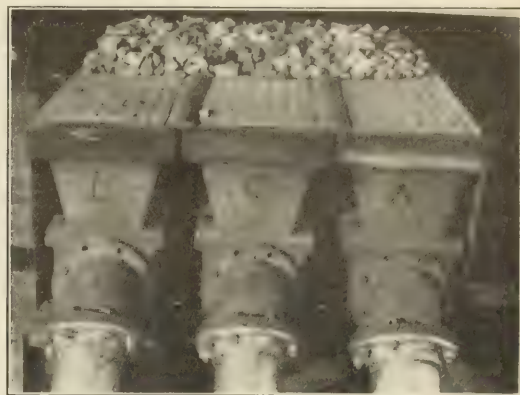


FIG. 24—VIEW OF THREE LARGE SOLID TYPE BURNERS, FORMING AN ACTIVE BED, 3 FT. SQ., CAPABLE OF BURNING 20,000 CU. FT. OF GAS PER HOUR

of fan blast and pipe connection. Mixtures were supplied through a twelve-inch header to three five-inch branches, one to each burner, and gas supplied through a six-inch main from the street was measured in a Wylie proportional meter, loaned for the purpose by the Equitable Meter Co. At 10 inches water pressure the rate would be 20,000 cu. ft. of gas per hour.

PROBLEM OF FEED HOLES

While the molding of groups of feed holes in tapered banks, long enough to keep the mixture chamber from reaching the ignition temperature, is a perfectly feasible mechanical construction and capable of insuring indefinitely long operation at any desired rate of combustion per sq. ft. of hearth, it has certain disadvantages that warrant a search for an improvement that will remove them. In the first place it is somewhat troublesome to mold the plastic material between casing and wires so as to secure a solid mass that will not crack on subsequent unequal heating, and when large these sections are very heavy and easily broken by shocks that may come when setting them in place. They are, moreover, necessarily high, too high for many locations, such as a cook stove or boiler furnace if present proportions of frames and settings are to be maintained. These with some others of minor value are sufficient objections to warrant a search for a better form though not serious enough to cause abandonment of this form if no better were available.

Fortunately a better form, and one that is completely satisfactory in all respects, has been found and it naturally follows from a little analytical reasoning. The holes through which the mixture is to be supplied must be cooled, and the cooling must be effective enough to keep the supply end above the temperature of ignition, but no more cooling than will do this is necessary or of value. In addition, the holes must be spaced at the hearth for proper distribution of heat

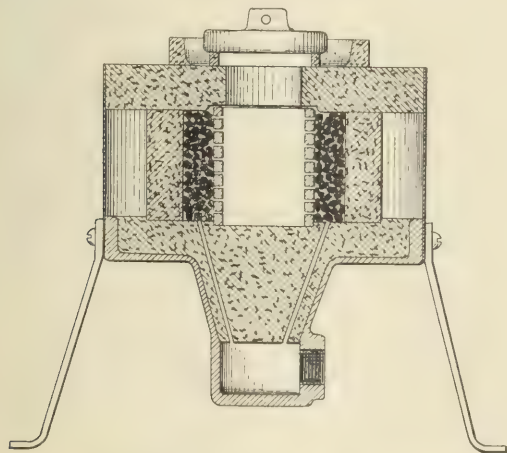


FIG. 23—CONSTRUCTION OF SMALL, SOLID TYPE MUFFLE FURNACE

three sections of wedge form, each 1 x 3 ft., make together a hearth of nine sq. ft. This burner was

and the desired rate of combustion per sq. ft. of hearth. Banking them in groups, as has been shown, will accomplish this, but it is clear that complete or partial structural independence of the holes by forming them in tubes so each may be cooled independent of the other or even forming them in ribs with independent cooling in at least two directions, is better and more effective than a form in which the heat to be dissipated from an inner hole must be conducted past an outer one also developing heat of its own.

PRACTICAL BURNERS

Accordingly, this principle has been incorporated, and burners constructed that seem, in every way, to

while pressing the lining in place, the cement forming a perfect hole in the hearth, exactly registering with



FIG. 28—SECOND FORM OF COOK STOVE BURNER; FIRE BRICK LINING IN PLACE AND LOOSE REFRACTORY FILLING

the drilled hole in the casting. Fig. 29 shows the completed burner with the granular bed in place, in this



FIG. 29—SECOND FORM OF COOK STOVE BURNER COMPLETE AND READY FOR OPERATION

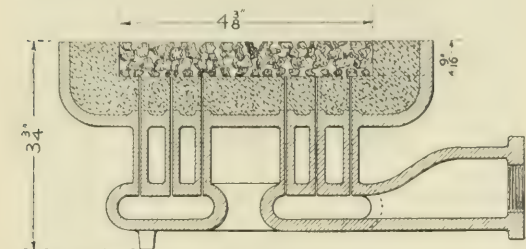


FIG. 25—SECOND TYPICAL FORM OF CONSTRUCTION OF ACTIVE COOK STOVE BURNER (TOP). HEAT DISTRIBUTION CONTROLLED BY SPACING FEED HOLES. RATE OF COMBUSTION BY NUMBER AND SIZE OF HOLES. LOCALIZATION BY VELOCITY REDUCTION AT OUTLET FROM HOLES AND BACK HEATING BY SEPARATE COOLING OF THE WALLS OF EACH HOLE

be satisfactory commercial forms for the essential element of all sorts of surface combustion apparatus. The construction of the first of these designed as a top burner for a domestic cook stove is shown in the

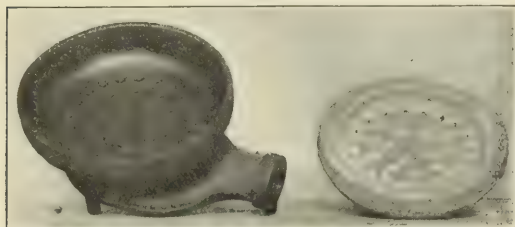


FIG. 26—TOP VIEW OF SECOND FORM OF COOK STOVE BURNER; CASTING BEFORE DRILLING AND FIRE BRICK LINING

sketch, Fig. 25, and photographically in Figs. 26 and 27, the casting and fire brick lining separate, and Fig. 28, the lining secured in place after drilling the feed holes



FIG. 27—SECOND FORM OF COOK STOVE BURNER; CASTING BEFORE DRILLING AND FIRE BRICK LINING

in each of the separately formed cast posts. To insert the lining, wires are inserted in the drilled holes

case crushed and sized fused silica. This burner has 35 holes each $1/16$ inch in diameter but other diameters

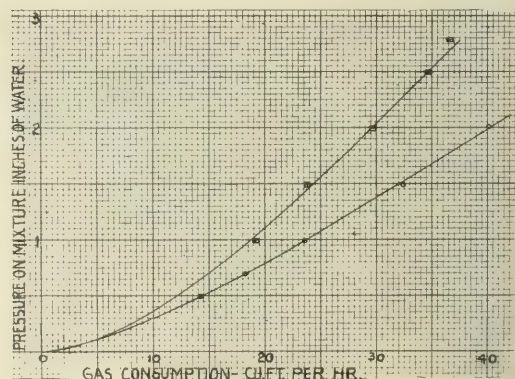


FIG. 30—RATE OF COMBUSTION AT VARIOUS PRESSURES ON CIRCULAR HEARTH OF COOK STOVE TOP BURNER, $4\frac{3}{8}$ " IN DIAMETER WITH 35 HOLES, EACH $7/64$ " IN DIAMETER FOR LOWER CURVE, $3/32$ " FOR UPPER CURVE

have been used, as well as other material for the bed of all sorts of thicknesses and while the consumption

and top temperature vary with each, practically everything works well and any result desired by the designer is obtainable merely by selection of suitable dimensions. In Fig. 30 are shown a pair of characteristic consump-



FIG. 31—RADIANT ROOM HEATER EQUIPPED WITH SECOND FORM OF TUBULAR TYPE BURNER, SET IN ORIGINAL SHELL OF STANDARD VULCAN HEATER. LOOSE BED HELD IN PLACE BY WIRE MESH NICHROME SCREEN

tion curves. Burners of this class have been thoroughly tested under both laboratory and kitchen service conditions, separately and as incorporated in complete cook stoves, having in addition inverted broiler burners with 60 holes, $\frac{1}{16}$ inch diameter in two rows and a long narrow rectangular hearth with loose granulated material held in place by wire mesh screens. Three of these placed in the top of the Vulcan hotel broiler shell gave consumptions of 38, 43 and 50 cu. ft. of gas per hour at pressures of 1 inch, $1\frac{1}{2}$ inches and 2 inches, respectively, all making a bright broiling heat that gives excellent service.

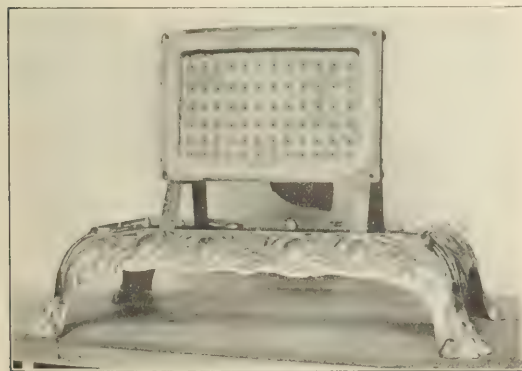


FIG. 32 RADIANT ROOM HEATER BURNER ON BASE WITHOUT BED OR SHELL

This screen construction is well shown by the illustrations of a curved face room-heater burner, designed

to fit in a Vulcan heater shell in the photographs, Figs. 31, 32 and 33. The first shows the new heater complete with an automatic proportioning mixing valve, to be described later, while the latter two show the burner without its bed, as set on the base and a separate side view. This burner has a rate of 14, $16\frac{1}{2}$ and $17\frac{1}{2}$ cu. ft. per hour at 1 inch, $1\frac{1}{4}$ inches and $1\frac{1}{2}$ inches pressure, respectively, on a hearth $8\frac{1}{2} \times 5$ inches = $42\frac{1}{2}$ sq. in. supplied with 72 holes, $\frac{1}{16}$ inch diameter, and in operation gives as strong a radiation of heat as is consistent with non-blistering of varnish on chair legs or ignition of carpet. While the refractory material is brightly hot, the No. 18 B. & S. four per inch wire of the screen does not seem to be above a faint dull red, and at this temperature all the alloys used in electric heater elements intended for operation at bright red heats up to 2000° F., without serious oxidation, will give good service in this location as will also common cast iron grids. Burners of any shape or size suitable for all sorts of household and hotel cooking and heating service can be produced along these lines to work in any position by the ordinary processes of design, involving no more complex mental processes than are required to select suitable materials and dimensions with the aid of established data or obtainable by simple experiment in any laboratory.

This same principle of supplying mixture through



FIG. 33 SIDE VIEW OF TUBULAR BURNER OF RADIANT ROOM HEATER

more or less independently cooled feed holes formed in metal walls and discharging into registering holes in refractory hearths, has been applied to higher rate appliances than those for domestic service such as the muffle and crucible service, and one each of these is shown by the photographs Figs. 34 to 36 both with feed holes drilled in ribs, which allows the same casting to be used for a wide range of capacities by changing drill sizes and center distances. The assay muffle is illustrated in Fig. 34, showing the two ribs carrying the feed holes with a few separate tubes placed at the side and front to develop enough extra heat to counteract the open front end muffle cooling, and equalize the temperature throughout the muffle. At the left-hand side is shown a single orifice sampling burner with open bed, consuming two feet of gas per hour and used to adjust the mixture proportions, slight changes in which are readily recognizable by the appearance of this small open fire. The main burner is operated normally at 110 cu. ft. per hour and with the above arrangement always gives a very

good thermal gradient, as shown by the following figures:

TEMPERATURE GRADIENT IN MUFFLE WITH FLUE AT FRONT

Top distance from front of muffle	Door closed	Door open
	No draft Temp. ° F	Good draft Temp. ° F
2"	1760	1600
4"	1870	1742
6"	1900	1820
8"	1910	1852
10"	1900	1840
Back 12"	1900	1820

The really significant thing here, however, is the ease with which any gradient desired can be obtained by changing the quantity of mixture supplied at differ-

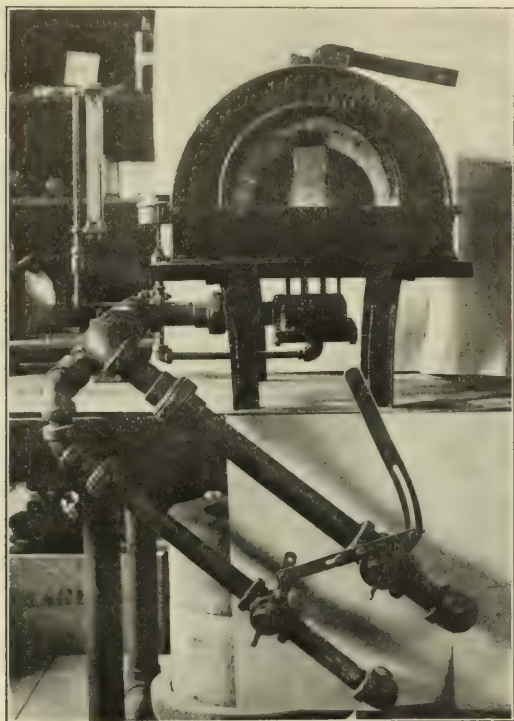


FIG. 34—FRONT VIEW OF MUFFLE FURNACE, SHOWING RIBS, CARRYING THE MIXTURE FEED HOLES

ent points, entirely independent of flue location. The crucible furnace shown in Figs. 35 and 36 is fed with two rows of holes drilled in a series of radial ribs and discharging in the annular space between insulation and muffle as can be seen in the first illustration with the top removed, which view also shows a sampling burner. The first view shows the side appearance and bottom mixture chamber from which the feed ribs run upward to the base, all cast in one piece. The mixture holes discharge into a hearth of alundum cement on which rests the cylindrical alundum muffle and after one run at about 10 inches water pressure, both muffle and hearth softened as shown by Fig. 37 on which the permanent shrinkage cracks clearly show as do also some pieces of white alundum that

adhered to both muffle and hearth. By a change of alundum bonding mixture both of these parts may be made more refractory, sufficiently so for a considerable

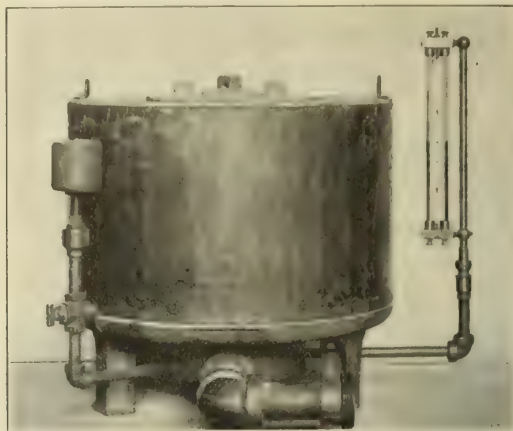


FIG. 35—SIDE VIEW OF CRUCIBLE FURNACE SUPPLIED BY HOLES DRILLED IN RADIAL RIBS BETWEEN MIXTURE CHAMBER AND FURNACE BOX. MIXTURE SAMPLING BURNER IS SHOWN AT THE LEFT

quantity of very high temperature work. It is not difficult, however, to consume, in such a furnace, enough gas to produce temperatures that will soften any available refractory, but by simply changing mixture pressures it is easy to maintain practically any temperature desired. If for any special purpose it should be necessary to maintain a secondary hot zone at any particular point, then separate mixture supplies can be led to that point and burn without interference with the products of combustion passing from another combustion zone, a condition peculiar to surface combustion, to which the well known "smothering" of common burner flames is unknown.

III. CONTROL AND ADJUSTMENT OF RADIATING SURFACE

By the application of the principles of construction so far developed, it is possible to make a surface com-



FIG. 36—TOP VIEW OF CRUCIBLE FURNACE WITH COVER REMOVED

bustion burner for any desired rate of combustion per sq. ft. of hearth that will operate for indefinite periods of time without disturbance or adjustment, but for

commercial apparatus even more than this is needed. One additional property that must be present is a suitable range of control of the rate, as few, if any, burners are operated in practice at a constant rate of combustion whether used for domestic or industrial purposes. It must be possible, therefore, to adjust the consumption of any burner from a minimum low, to a maximum high rate and to operate safely and surely at any one, no matter what the previous adjustment or the time of operation. Furthermore, some classes of service require a very prompt change in the radiating bed temperature after adjustment, which includes a very quick initial heating after lighting cold, while other classes of service require a slow change after adjustment or a sluggish response to changes. With any given range of adjustment of rates for safe working,



FIG. 37—SIDE VIEW OF CRUCIBLE FURNACE MUFFLE AND HEARTH, SHOWING THE EFFECT OF SOFTENING OF MUFFLE BY HEAT. MATERIAL OF BOTH, ALUNDUM MIXTURE

there may be associated the requirement of a prompt or a sluggish response after a change, but fortunately in no one burner is it ever necessary or even desirable to provide for more than a limited range of adjustment associated with either prompt heating or sluggish, never both. These conditions can be met in the sort of burners described sufficiently well to meet practically all service requirements consistent with maintaining the advantages of surface combustion as a process.

RANGE OF CONTROL OF RATE OF COMBUSTION

The range of control of rate of combustion depends primarily on the size of the feed holes and on the effectiveness of their cooling, and it is easily possible to make holes small enough in separate tubes or ribs to absolutely prevent back flash even when the mixture is turned off and the velocity of flow reduced to zero. By imposing sufficient mixture pressure on

enough of these holes per square inch of hearth, any maximum rate of combustion may easily be associated with this minimum rate of zero. Certain practical considerations such as the extra cost of forming small over large feed holes and the increased possibilities of stoppages in them make it desirable to use larger holes than correspond to a minimum rate of zero when that is not necessary, and it has been found that holes $\frac{1}{16}$ inch in diameter are small enough for safe operation at rates as low as most service requires. Holes of this size in cook stove top burners, broilers and room heaters, can be safely operated at two- or three-tenths of an inch pressure, giving thereby at least as great a range of adjustment as is possible with Bunsen burners of the ordinary form without back flash. Such holes seem to keep free of stoppages and are cheap to form if not much over one inch in length. Apparatus intended normally for much higher rates than the domestic class would naturally be given larger holes, and, therefore, have a higher minimum operating pressure, but the range desired even with this higher minimum is easily obtained by using a correspondingly higher maximum. Thus while the maximum pressure available for operating domestic apparatus without gas boosting, which is out of the question here, is a little less than that of the street main, say 3 inches of water, that for an industrial furnace for which gas boosting is not objectionable may be made even with small fans as high as 12 inches and with positive blowers several pounds. Assuming the holes in the latter case to be such that the minimum safe pressure is 1 inch, there is a pressure range of 12 : 1 for adjustment of rate. Correspondingly, if the domestic apparatus has a minimum safe pressure of 0.2 inch, then it has an adjusting pressure range of 15 : 1. It must not be understood that these are limiting figures, for they are not, being offered merely as examples, since the real range may be made whatever is desired, a thing thought to be impossible in the early days of surface combustion development.

TIME OF HEATING

The time of heating is likewise within control though not through so wide a range; *i. e.*, by adopting suitable constructions the burner may be made to heat up from the initial cold to the normal working state in a short or long time, and will be correspondingly quick or sluggish in response to pressure rate adjustments while in operation. Sluggishness is obtained by using a thick bed of great mass and, therefore, large heat storage capacity, while sensitiveness follows the use of beds or radiating surfaces as light as possible. It is clear that, taking for example the cook stove top burner, a bed only $\frac{1}{4}$ inch thick will heat quicker and respond more positively to valve adjustments than a bed 1 inch thick, other things being equal, and the time of heating the latter would approximate four times that of the former if there were no interfering influences. These influences are, however, present and are somewhat difficult to understand at first, but clear enough after study.

In the first place, a reduction in the thickness of bed may leave it so thin that it is no longer effective

in reducing mixture velocity at the hearth orifices, so that mixture will blow off at various points where the grain does not properly baffle a jet. The escape of this mixture actually reduces the heat developed in the bed, delays its heating and so counteracts the expected gain from bed mass reduction; at the same time it causes a smell from the escape of the unburned gas which, of course, ceases once the bed is heated even when the baffling is very poor. This is one of the difficulties encountered in the effort to reduce the initial heating time by reduction of bed thickness. It would seem that if, starting with grain $1/4$ inch in diameter a reduction of bed thickness was carried so far as to cause partial blow off by insufficient baffling, this could be corrected by a reduction of size of grain and this is so, but here again limits are met. In no case may the grain be so small as to fall into the end of the tube, but with small holes used, even before this occurs two other things are noted: (1) A thin layer of fine grain on the flat hearth will not heat uniformly with the hole spacing satisfactory for larger grain; a series of bright spots above each hole with dark areas separating them will replace the uniform color of a thicker and, therefore, more sluggish bed. (2) The fine grain bed will not heat initially in the same way that the coarse one will, for below a certain grain size the combustion locates initially on the outside surface, which heats first, the combustion zone gradually working back toward the orifices, while with a larger grain, offering fewer and wider mixture passages in the voids, the combustion zone locates instantly about the holes, flashing directly through the bed. In other words, the fine grain bed heats from the surface *inward* while the coarse heats from the inside *outward*, and though for two such beds of equal weights of material it would seem that equal times must elapse before each had reached a steady state, as a matter of fact the one that heats first from the outside will be quicker because of the non-escape of unburned mixture while heating.

QUICK HEATING TOP BURNERS

This reasoning leads naturally to one of the successful forms of quick heating top burners which becomes incandescent and uniform at the normal rate of combustion in about half a minute, the ordinary half-inch thickness of large grain bed requiring three to four minutes, depending on the material. This one is formed by counter-sinking the outlet side of the $1/16$ inch feed holes to $1/2$ inch, filling the tape holes with silica of size $10/64-2/64$ inch, and also covering the hearth to a depth of $1/4$ inch, as indicated in the sketch, Fig. 38.

Reduction of mass to be heated without interference with the effectiveness of the baffles and by using materials that are permanent is a definite problem for which there are many solutions and no doubt others will appear as long as specific attention is given to it, but it is a serious question whether reduction of time below one minute, or even to this time, is really advisable. There is available one type group of construction already explained under localization, and that is the formed baffle, of which the flat plate mushroom

plug and ball in tape hole are examples, and over which may be placed the radiant screen, of metal, perforated or woven, a thin layer of loose grain, or a diaphragm of refractory perforated or otherwise formed, to be porous enough to allow the free passage of gases; all these have been used as well as some others that proved unsatisfactory. In the latter class fall a layer of picked asbestos fiber which heats as quickly as an illuminating mantle but which has no life; a $1/4$ inch layer of hollow cylinders or short thin silica tubes like straight beads, $1/8-1/4$ inch diameter and $3/8$ inch long, which heats in less than one minute and is permanent but too expensive; and a thin plate of alundum cement perforated freely with $1/8$ inch holes, which becomes incandescent in one minute but is too fragile. In the former class fall the perforated metal non-oxidizing alloy plate over some form of direct baffle, and the molded porous diaphragm directly over the holes serving as both baffle and radiator, the former giving a very quick heating but not so permanent as the latter

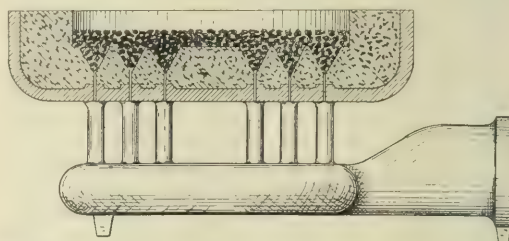


FIG. 38—MODIFICATION OF TUBULAR TYPE COOK STOVE TOP BURNER FOR QUICK INITIAL HEATING

which, however, heats more slowly. For the metal plate, two materials have been used, Nichrome II and Excello, the analyses of which are given below, as determined by Whitaker and Metzger:

ANALYSIS OF NON-OXIDIZING ALLOYS (PERCENTAGES)

Nichrome II		Excello	
Sample No. 1	Sample No. 2		
Nickel.....	56.4	Nickel.....	83.43
Chromium.....	10.6	Chromium...	14.72
Iron.....	30.6	Iron.....	1.30
Manganese.....	2.1	Silica.....	Trace
	99.7		99.45

The former has been most used and as applied to the problem of quick heating was in sheet form, 0.032 inch thick, perforated with holes 0.073 inch diameter and about one diameter apart. This was cut circular to fit the top burner hearth $4\frac{3}{8}$ inches diameter and heats to normal in about half a minute when set over baffles of the mushroom or plate type, and in about ten seconds with ball baffles. Such plates have a fair life if not operated at too high a temperature; about one cu. ft. of gas per hour for each two sq. in. of radiation is a satisfactory rate and gives a good red heat. This construction may, therefore, be adapted as a direct competitor of the electric heater, using the same radiant material at the same temperature, but with gas as the source of heat instead of electric current. A series of consumption curves of one of these quick heating nichrome radiating plates, $4\frac{3}{8}$ inches di-

ameter, set over 35 holes, $\frac{1}{16}$ inch in diameter, in the cook stove top burner hearth with mushroom baffles plugs is given in Fig. 39.

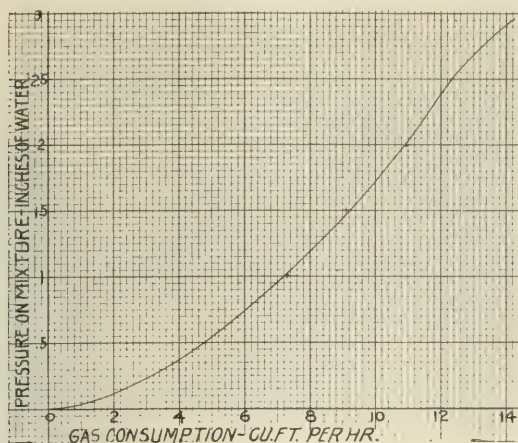


FIG. 39—RATE OF COMBUSTION OF TUBULAR TYPE COOK STOVE TOP BURNER HAVING 35 HOLES, EACH $\frac{1}{16}$ " IN DIAMETER, DISCHARGING UNDER SQUARE STEMMED MUSHROOM PLUGS, SHOWN IN FIG. 3 AND PROVIDED WITH PERFORATED NICHROME RADIATING PLATE

REDUCTION OF HEATING TIME

It is a serious question whether the reduction of heating time should be carried so far, even in domestic apparatus in spite of a demand on the part of users for it, because of the corresponding small heat storage. The top burner carrying a half-inch loose bed has so much heat storage that it will resist interference from the spilling on it of large quantities of water or grease, amounts of which sufficient to be serious with Bunsen burners have no effect here whatever, but the more this heat storage is reduced by constructing for quick heating the less this resistance. Another advantage of heat storage in the incandescent bed is inherent in all intermittent heating such as the heating of laundry irons, which may thereby absorb heat for a time faster than it is being generated by drawing on the bed storage; these always heat faster on the surface combustion burner than on a common burner of equal gas consumption. One trial showed that with two irons on a surface combustion burner a laundress could do as much work as with three irons on the Bunsen, the former consuming about half the gas that the latter used and heating the iron in less time.

INFLUENCE OF SERVICE CONDITIONS

In applying these surface combustion burners a new study of service conditions is necessary as they have some characteristics, not possessed by the old burners, that permit and even demand adaptation of burner design to service. There will always be some cases where quick heating is important, *e. g.*, in toasters; others where heat storage is important; top burners for intermittent service and those that are much used and likely to receive spillings; also others that will demand the smooth self-supporting surface of the bonded diaphragm, which is operative in all positions and which has properties all its own.

USE OF DIAPHRAGMS

The application of the bonded diaphragm to general service conditions is a problem in itself, as the localization of combustion is not so readily controlled under wide ranges of mixture pressures within the limits imposed by the ordinary domestic gas service. All such diaphragms except those of very great porosity and, therefore, necessarily thick, will heat from the outside inward and in all, the heat will work back, the combustion zone following until back flash takes place under some supply pressures and times of heating. Assuming that general service apparatus will be operated at a variable rate and at such variable pressures, the localization combustion by diaphragms is not to be depended upon; but they will still be useful as baffles and radiators when placed over a hearth, such as described, and which latter insure localization.

Placing a bonded diaphragm over such a hearth as that of the cook stove top burner, it will, on ignition, heat from the outside first; the combustion zone will then work down and through it until a back flash occurs and the combustion zone locates between the hearth and bottom face, extending from each hole into the diaphragm a little way if it lies directly on the hearth. As the heat works back unevenly, due to non-homogeneity of voids and size of grain, there will be at the moment of ignition below it only one hot spot, all the rest of the bottom and the hearth being cold. Up to this moment the outer surface has been hot and radiating, but now the heat will be practically all absorbed by the hearth and lower space until they become incandescent, and in this period the top radiating surface will cool and then slowly recover its temperature, after which it will operate indefinitely without change. The time it takes for the outer surface to begin to radiate, and for the back flash to occur are both dependent on the relation of porosity to pressure or rate of supply, but the time of recovery after back flash is largely controlled by diaphragm uniformity. If the combustion zone works back equally fast all over the diaphragm the bottom face will be hot all over when bottom ignition takes place, instead of only one spot, and thus the top temperature will be recovered most rapidly.

A great many small diaphragms of all sorts of grain materials and bonds have been tried and all abandoned in favor of alundum; these have been prepared by the Norton Co., to whom considerable credit is due for the spirit of cooperation displayed in opening up a new field, absolutely without data. Without reciting the details, it may be noted that satisfactory results are obtained with Norton alundum diaphragms fed through the self-cooling mixture holes and set over the discharge hearths. These are structurally quite strong if the bond used is not intended for very high temperatures, in which case they are delicate but still useful for some purposes. Two consumption tests of such diaphragms set in the hearth over 35 holes, $\frac{1}{16}$ inch diameter, the porous part being 4 inches diameter and $\frac{1}{2}$ inch thick, are given in Fig. 40, comparing a Norton alundum diaphragm of No. 4 grain with an English fire clay diaphragm, which latter fused in

time on the hearth side, the former remaining unchanged. In Fig. 41 are given similar results for a series of alu-

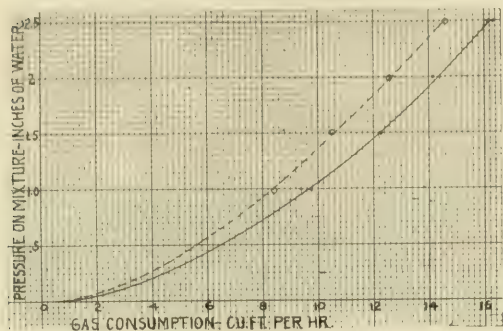


FIG. 40—RATE OF COMBUSTION OF COOK STOVE TOP BURNER HAVING 35 HOLES, EACH $1/16$ " DIAMETER, DISCHARGING TO BONDED DIAPHRAGMS. TOP CURVE DIAPHRAGM OF NORTON ALUNDUM MIXTURE. BOTTOM CURVE ENGLISH FIRE BRICK MIXTURE

dum diaphragms $5\frac{1}{8}$ inches diameter, $7/16$ inch thick, set over the same hearth after enlarging. These were of four sizes of grain No. 8, No. 6, No. 4 and No. 2, and three different processes of working. Change

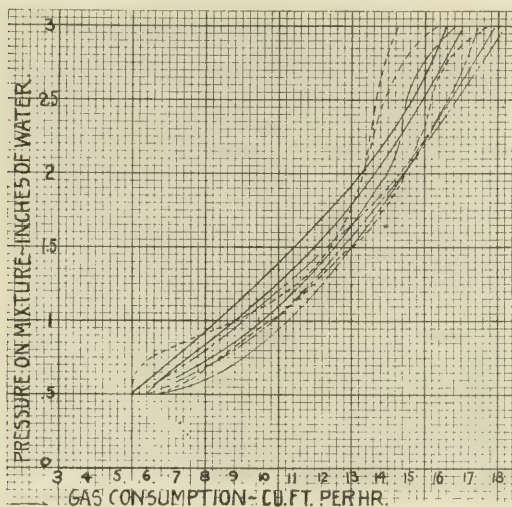


FIG. 41—RATE OF COMBUSTION OF COOK STOVE TOP BURNER HAVING 35 HOLES, EACH $1/16$ " IN DIAMETER, DISCHARGING THROUGH NORTON ALUNDUM DIAPHRAGMS OF DIFFERENT CONSTRUCTION. EACH DIAPHRAGM $5\frac{1}{8}$ " DIAMETER AND $7/16$ " THICK. VARIATION IN CURVATURE SHOWS TRANSFER OF MAIN RESISTANCE FROM FEED HOLES TO DIAPHRAGM

of curvature indicates that the main flow resistance has been transferred from feed holes to diaphragm.

The time of back flash and recovery of surface temperature varies considerably but in the best the whole time is about five minutes; in some cases it has reached 15 and even 20 minutes. The time of recovery varies from 3 to 12 minutes, the better diaphragms requiring the lesser time, all at pressures of $1\frac{1}{2}$ inches of water.

IV. AUXILIARY APPARATUS

Any burner or furnace intended for laboratory use where operators have sufficient skill and understanding of cause and effect, need not be supplied with any special appliances for proportioning air to gas in the mixture, or for changing the mixture pressure as service conditions require it and, therefore, any of the many standard fans and blowers may be used for compressing air alone or air and gas separately with a hand-adjusted cock in the air and the gas pipes supplying each appliance. This is by no means the case, however, with some industrial and with all domestic appliances. Where an industrial furnace operator is more or less constantly engaged in managing one furnace, he can be taught to make adjustments of hand valves if provided with the ordinary water column water gauge and a small sampling burner, but this is entirely out of the question for the ordinary woman in the home or chef in a hotel, as they either cannot or will not adjust anything beyond turning the cock that regulates the heat and it must be confessed, sometimes not even this. For domestic service, including that of hotels and restaurants, it may reasonably be expected that they operate a single cock for each burner to regulate the heat, but maintenance of mixture proportions essential to surface combustion processes must be automatic and fool-proof. This at first, like some of the other questions taken up, looked like a difficult problem yet it seems to be working out in a thoroughly satisfactory way.

AUTOMATIC MIXTURE PROPORTIONING

Automatic mixture proportioning has been accomplished by two devices which working together carry out the fundamental method; *i. e.*, proportioning by equal pressure drop on an air and a gas orifice, having areas in the desired proportion. Regulation of air pressure to an equality with that of the gas supply available at the appliance will bring them to a control

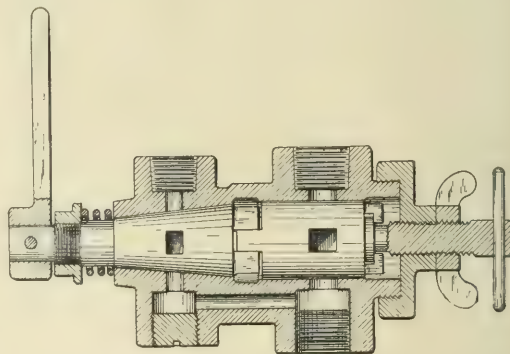


FIG. 42—SECTIONAL VIEW OF DOUBLE-PORTED MIXING VALVE, WITH ADJUSTMENT FOR RATIO OF AIR TO GAS

cock having two ports with areas in the desired proportion and by suitably large pipes or small port openings; these ports determine the flow to a common mixture outlet, and the proportions will remain constant so long as the principal resistance to the flow of both

is in the cock ports. This is accomplished, first, by sufficiently large supply pipes but it is necessary also that the ports bear a suitable relation to the burner opening so that while the pressure drop through the burner is large enough to establish the desired veloci-

tion at the left. This has two plugs, keyed together so as to rotate together, but otherwise free; one, carrying the small gas port, is tapered and spring seated for tightness, while the other, carrying the air port, is cylindrical, and has an axial adjustment for length



FIG. 43—DOUBLE PORTED ADJUSTABLE MIXING VALVE; COMPLETE AT THE RIGHT AND IN VARIOUS STATES OF ASSEMBLY AT OTHER POINTS

ties for localizing the combustion zone, there is also some drop of pressure through the ports themselves. In other words, the combined area of the ports in the wide open position must never be so large as to build up in the mixture chamber a pressure equal to that in the air and gas supply pipes. This does not involve any serious drop through the ports; two- or three-tenths of an inch of water is ample, and less will do if necessary, but the more there is the more definite the proportioning and incidentally the smaller the valve needed. To permit of an adjustment to changes of gas quality one port may be made of fixed size with the other adjustable, but in opening and closing both must vary in constant ratio. It is not expected that users will make this quality adjustment, but rather the gas men who make installations and, of course, in any one district a setting will be found good for the average air requirement of the sort of gas supplied, the variation in which is never large enough to seriously interfere with the operation on this mean setting. Wherever the gas is uniform or substantially so, in air requirements, this gas quality adjustment can

of effective opening to adjust for gas quality. Both plug ports are aligned with the casing ports so as to absolutely open and close together. With this cock, the user regulates the burner exactly as has been the case with common burners, controlled by single ported cocks.

CONTROL OF PRESSURES

It is necessary, however, for the satisfactory working of any form of double ported cock, intended to maintain constant proportions of air and gas while controlling the total quantity of flow from zero to a maximum, that the air and gas approach at equal pressures

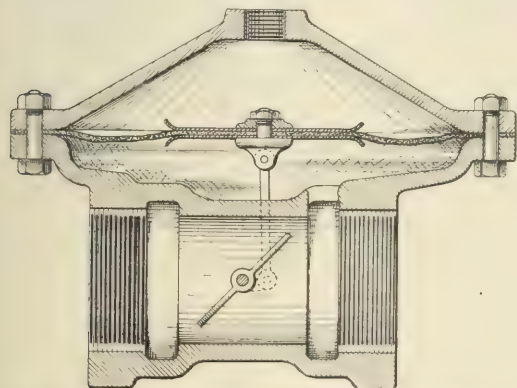


FIG. 44—SECTIONAL VIEW OF AIR PRESSURE REGULATOR FOR MAINTAINING AIR PRESSURE EQUAL TO THAT OF GAS

be eliminated and the ports fixed at the proper value, once for all. One successful cock of this sort is sketched in Fig. 42 and shown photographically in Fig. 43, complete on the right and in various stages of dissec-

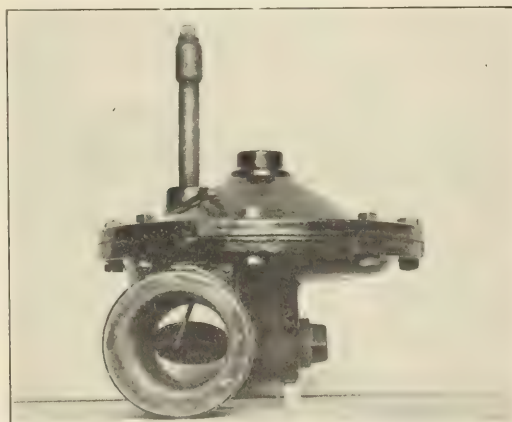


FIG. 45—VIEW OF REGULATOR COMPLETE; CONTROL DAMPER HELD OPEN BY A KNIFE

so that the drop in pressure to the common mixture pressure be equal; this may be accomplished by regulating the air pressure to that of the gas, or conversely. The former has been used as most satisfactory, and in accordance with it, the air delivered by the fan is passed through a diaphragm regulator carrying a damper valve in the main air passage. This damper is rotated by a crank and connecting rod, fixed to the meter leather diaphragm, the weight of which is balanced by a spring or dead weight, if horizontal, but is

to be neglected if operated in a vertical plane. The delivered air pressure is caused to act on the bottom of the diaphragm while the local gas pressure acts above; both sides, being dead ends, that is, not swept by any current, there is little tendency to dry the leather. All changes of gas pressure vary the diaphragm load and move the damper to the position for re-equaliza-

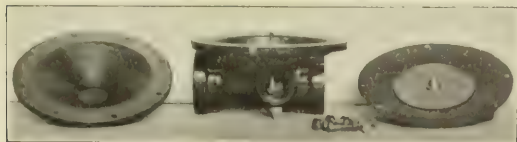


FIG. 46—AIR PRESSURE REGULATOR PARTLY ASSEMBLED, SHOWING AT THE CENTER CONNECTING ROD AND CRANK FOR ACTUATING THE DAMPER BY THE DIAPHRAGM MOVEMENT

tion promptly and positively so that no matter how local gas pressures may vary, the air automatically follows and the mixture quality remains what it should be. The construction of this regulator is shown by

tion of these surface combustion appliances but the pressure need be no more than is necessary for good regulator action, for which about 1 inch water drop is desirable. Air pressures of this order of magnitude are easily obtainable by fans and are preferably, though not necessarily, electrically driven. If the full available gas pressure is used, and this be three inches, then the fan should deliver at four inches of water, but very satisfactory operation can be secured at mixture pressures as low as 1.5 inches, for full capacity, which would require less than two inches of gas pressure and less than three inches fan delivery. At such pressures the power requirements of the fans for ordinary appliances are very small, as may be easily calculated. For quick reference, the results of such a calculation are given in chart in Fig. 47 for a wide range of capacities and pressures, to which is added a scale for reading motor horse power for any fan efficiency and electrical input horse power for any electric motor efficiency. For small sets the fan efficiency will probably be between 30 and 50 per cent, while

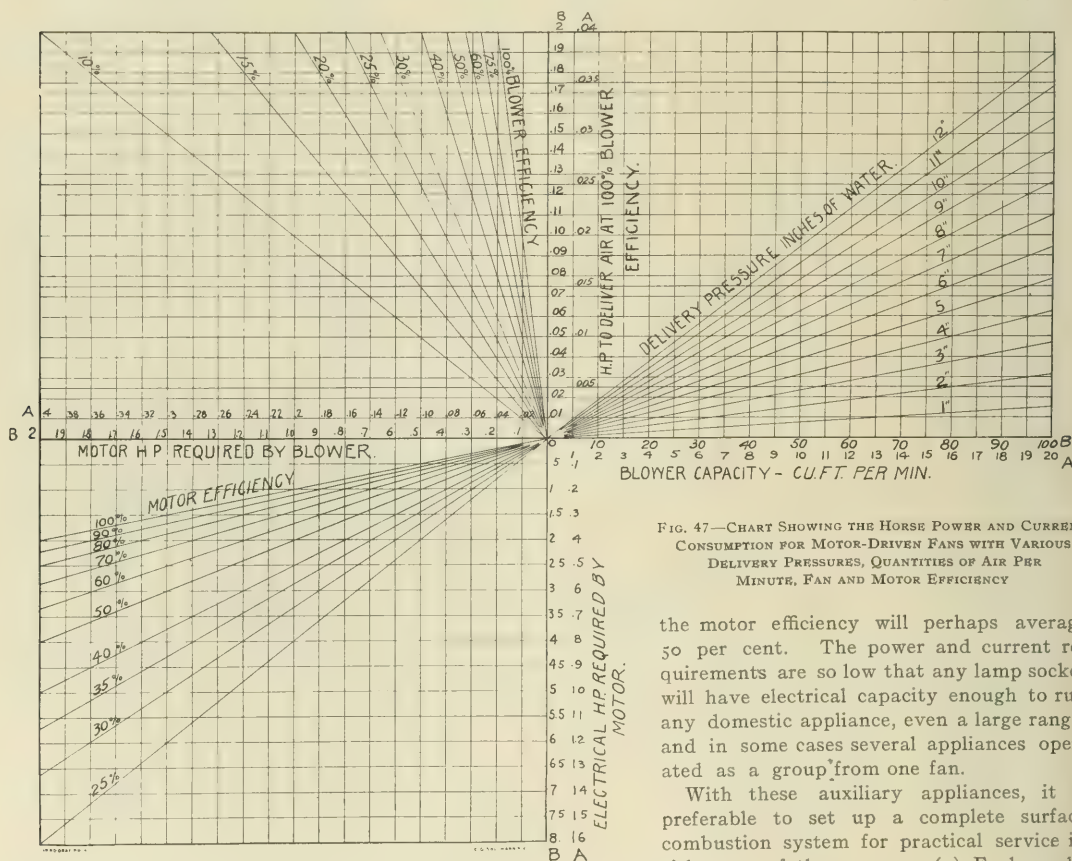


FIG. 47—CHART SHOWING THE HORSE POWER AND CURRENT CONSUMPTION FOR MOTOR-DRIVEN FANS WITH VARIOUS DELIVERY PRESSURES, QUANTITIES OF AIR PER MINUTE, FAN AND MOTOR EFFICIENCY

the sketch, Fig. 44, and the two photographs, Fig. 45 showing one size of regulator complete, and Fig. 46 showing it partly dissected.

AIR PRESSURE NECESSARY

Air under pressure is always necessary for the opera-

the motor efficiency will perhaps average 50 per cent. The power and current requirements are so low that any lamp socket will have electrical capacity enough to run any domestic appliance, even a large range, and in some cases several appliances operated as a group from one fan.

With these auxiliary appliances, it is preferable to set up a complete surface combustion system for practical service in either one of three ways: (1) Each appliance with its own fan and regulator and so completely independent except for connection to gas and electric service mains. (2) A central fan with distributing air pipes to each appliance with its own regulator. (3) Combinations of appliances in groups.

It is comparatively easy to see how central or group systems would work out for large installations suitable, for example, for hotel kitchens, but it is a matter of some interest to examine the independent domestic unit.

FIRST SURFACE COMBUSTION RANGE

The first of these ever constructed was made by converting one of the standard side cabinet ranges now on the market, using mixing valves that had been used elsewhere and a fan taken from a vacuum cleaner, in the absence of one of suitable capacity as to volume and pressure. The fan used was that of the Regina cleaner in one casing with a G. E. motor and had an air volume capacity about four times what was needed, delivering at about 11 inches of water where four or five would have been sufficient; it consumed 90 watts with all burners in operation. These things are stated to explain the somewhat crude appearance of some parts of this, the first self-contained surface combustion range ever constructed and put into service in a home kitchen. In Figs. 48 and 49 all parts are clearly shown,

to provide for the flow of a smaller volume of gases at higher temperatures with the surface combustion burners than with the original Bunsen burners.



FIG. 48.—DIAGONAL TOP VIEW OF FIRST DOMESTIC RANGE; SOLID CAST IRON TOP, WITH FOUR TOP BURNERS; REFRACTORY IN PLACE BUT BURNER GRID REMOVED

except the check valve between fan delivery and regulator to prevent gas escape from the fan, should a burner be turned on when the fan is not in operation; this was not at first provided. It will be noted that the mixing valves or double ported cocks are fitted with graduates to guide the operator in adjustment, as the absence of visible flame, the ordinary guide, here demands a substitute. All auxiliary or secondary air openings into the oven are closed as now unnecessary and if left tending to reduce efficiency by the air so drawn in and discharged hot to the flue. For the same reason the chimney vent is made smaller. The oven flue linings were not changed but should have been

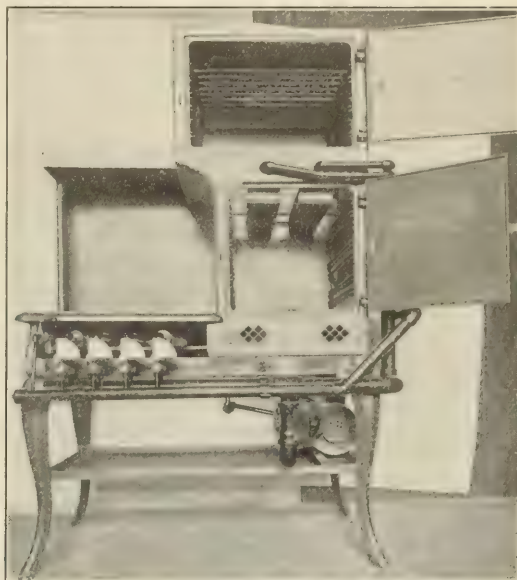


FIG. 49.—FRONT VIEW OF FIRST COMPLETE DOMESTIC RANGE, WITH OVEN DOORS OPEN. BROILER AND OVEN BURNERS ARE VISIBLE, EACH BEING RECTANGULAR, MIXTURE SUPPLIED TO HOLES DRILLED IN RIBS BETWEEN MIXTURE CHAMBER AND HEARTH. BURNERS ARE SUSPENDED FROM FRONT AND BACK WALLS. THE CLOSING OF THE OPENINGS FOR SECONDARY AIR IS ALSO VISIBLE ON THE LOWER DOOR, NO SECONDARY AIR BEING NEEDED FOR THE SURFACE COMBUSTION PROCESS

V. EFFICIENCY OF SURFACE COMBUSTION APPLIANCES COMPARED WITH BUNSEN

As in other cases, it is here found that the absolute and relative efficiency of surface combustion and Bunsen burner appliances is not a constant thing but varies with conditions and, therefore, any discussion must be more or less limited in scope to give a correct impression. For this reason the figures obtained from tests will be confined to domestic appliances operating on city gas, such as cook stove top burners, broilers, oven, room and water heaters, all made by removing Bunsen burners from standard appliances and substituting the new ones. Top burners were tested by taking the consumption and time to raise a weighed body of water to 200° F., from an initial low temperature; the same or identical vessels always open were used in all comparative tests.

From a large mass of tests conducted with various bed materials and thicknesses, different sizes, shapes and materials of vessels, different distances between bed or flame and the vessel, at all sorts of gas or mixture pressures at various positions of the cocks and with various stove, top or burner ring construction, the figures themselves vary so much as to be at first perplexing to one seeking some definite, general conclusion on the relative value of the two systems. Careful analysis, however, reveals some order from which conclusions follow relating results to conditions. The

first of these is that with identical conditions or as nearly so as the differences in the systems permit, the surface combustion burners always do an equal amount of heating of the water with less gas than the Bunsen but how much less seems to be dependent on the construction of burner, stove frame and water vessel. Perhaps the most important of these external conditions is the vessel itself, and however queer this may at first seem, an explanation is available. If the vessel be large, of good conducting material, like copper or aluminum, and containing a large amount of cold water, it would approximate the heat absorber of a gas calorimeter and could take up a very large amount of the heat being generated at a given rate. On the other hand, if the vessel has a small heat-absorbing surface in proportion to the rate of combustion and be made of poor conducting material then there is less chance of heat being taken up by the water, other things being equal. Size and material of vessel placed over a burner developing heat at a given rate do, therefore, determine, to some extent, the rate of heat absorption, but also the rate of heat dissipation from its sides, both the submerged and exposed part, and the water surface. This last factor is also more or less influenced by the extent to which the vessel is filled and the air drafts blowing on it. It thus appears that a great deal depends on the vessel and its filling, but as many detailed figures are always confusing the results of two vessels only are given in this connection.

One of these is a cylindrical tinned iron sauce pan, about 8 inches in diameter and of equal height and the other a smaller tapered pressed steel enameled sauce pan, about $6\frac{1}{2}$ inches in diameter, both tested on New York City gas, over burners consuming 15 cu. ft. per hour, the Bunsen burner being of the Crane construction and the surface combustion having a $4\frac{3}{8}$ inch hearth with $\frac{29}{64}$ to $\frac{24}{64}$ inch material, $\frac{1}{2}$ inch deep and covered at the edges by a cast iron ring with vents between it and the vessel $\frac{1}{8}$ inch wide. For equal amounts of heat taken up by the water the relative consumption was as follows:

Bunsen burner consumption = $1.44 \times$ surface combustion burner consumption with large iron pot; $1.66 \times$ surface combustion burner consumption with smaller enameled pot. These two burners turned down to a simmer, using the enameled pot and keeping the water just below the boiling point as nearly as could be judged by the eye, the consumptions were: Bunsen 5.2 cu. ft. per hour and surface 2.42 cu. ft., giving the ratio of 2.15.

The average of the two other series with enameled vessels on Westchester, N. Y. gas, a thick silica bed surface combustion stove, grid top, 15 cu. ft. per hour, with a G. G. A. Co. Bunsen burner, gave consumption ratios of 1.71 and 1.75. A different surface combustion burner, that designed for quick metal heating becoming normal in less than one minute, as compared with three or four minutes for the above burners, and illustrated in Fig. 38, gave a ratio on N. Y. C. gas of 1.80. This last was also fitted with a grid top, the enameled vessel being held about $\frac{1}{2}$ inch above the bed.

These are high values and indicate a large fuel consumption as may be seen from the following figures: Assuming a Bunsen burner to be consuming 15 cu. ft. per hour, then to give the same heating effect in a cooking vessel, the surface combustion burner for consumption ratios of 1.8, 1.7, 1.6, 1.5, 1.4, and 1.3 would require 8.3, 8.8, 9.4, 10.0, 10.7 and 11.5 cu. ft. per hour, saving 6.7, 6.2, 5.6, 5.0, 4.3 and 3.5 cu. ft. gas per hour while doing the same work. The high ratio above reported as actually attained may not be under favorable conditions and low values have frequently been found; in one case lower efficiency with a certain surface combustion burner and top construction than with the Bunsen; but this fact pointed out the mistake in construction which, when corrected, resulted in high ratios. As has already been pointed out, the size of vessel is important but so also is the heat dissipation from the top. In one case a solid stove top was used with circular openings to take the burners and quite low efficiencies were obtained, as low as 1.2, but it shortly appeared that most of the hot gases were escaping along the underside of the cold top instead of rising around the vessel, due to bad construction. A simple substitution of a grid that allowed the gases to rise with no other change raised the ratio from 1.2 to 1.68.

GAS SAVED BY NEW PROCESS

It may easily happen that service conditions will arise that will demand constructions that are not highly efficient as, for example, cold cast iron tops for intermittent service, in the interest of cleanliness, so that a commercial stove construction will probably be a compromise. The best judgment that can now be made is that, taking into consideration all these conditions, there may be expected a consumption ratio of about 1.55 Bunsen to flameless, or 0.65 flameless to Bunsen, which indicates a saving of about 35 per cent of what is now being used though it is possible according to actual tests that it may be as high as 45 per cent.

EFFECT OF EXCESS AIR

It has previously been stated that the expected savings from the surface combustion process were to be derived first from the elimination of the excess air now required of all Bunsen burners, and second by the superior penetrating power of radiant heat in warming bodies from the fire. The influence of these two together is well shown in all the preceding relative consumptions but perhaps nowhere quite so well as in the case of the simmering test where two fifteen-foot burners were turned down to keep the water just at the boil for about one hour, which raised the consumption ratio from 1.66 to 2.15. This is a splendid demonstration because in the turned down condition very much more cold air rises with the hot flame gases to the pot bottom in Bunsen burners than when they are on full while there is no change, whatever, in this respect with the surface combustion burner. The difference above is, moreover, largely due to excess air because at the turned down condition the surface combustion burner bed was only faintly radiant.

The minimum effect of this excess air influence is perhaps best obtainable from a comparison of two water heater tests made on identical coils of the Vulcan heater, one as constructed with standard Bunsen burners and the other with a surface combustion burner substituted, but without other change. Both were operated to heat the water in a standard forty-gallon copper tank, equipped with thermometry and the results are uncorrected for radiation from it or pipes. On an assumed calorific value for the gas, the Bunsen burner gave an efficiency of 70.4 per cent, while the surface combustion burner gave 82.3 per cent, a ratio of 1.17, the flue gas temperature of the Bunsen being 248° F. against 309° F. or 61° higher, for the surface with its excess of 12.3 per cent efficiency. Of course, a properly constructed surface combustion heater can easily be made to yield as close to 100 per cent efficiency as may be desired; these figures are given not to show what may be expected of such, but purely as a measure of the excess air influence when it is reduced to its lowest value in the Bunsen equipment; this condition is entirely eliminated by surface combustion.

Another measure of excess air influence is given by the figures for a comparative top oven test in which an upper oven was heated by burners below, intended primarily for a broiler oven below, Figs. 48 and 49. As originally equipped with Bunsen burners this top oven required 19 cu. ft. of gas per hour to maintain at its center a temperature of 480° F., as against 13.5 cu. ft., a ratio of 1.4, when surface combustion burners were substituted, with no other change than the closing of the secondary air openings, linings which should have been changed being left in place.

VALUE OF RADIANT HEAT

The direct value of the radiant heat developed by surface combustion burners is shown most clearly in test of such apparatus as a broiler, or a radiant room heater, Fig. 31. Tests have been made in such broilers by taking the consumption for the proper cooking of steak and chops, both thick and thin, chicken, squab, fish, lobster, and toast, under the direction of competent chefs, and comparing with that required for the same carefully measured and weighed in Bunsen burner broilers. For this purpose was selected the Crane Bunsen burner broiler with cast iron fingers heated to a dull red by the flame, thus giving more radiant heat than other types not so provided though more commonly used. This was done to provide the most vigorous Bunsen burner competition available as a basis of comparison for the surface combustion burner and the results varied in specific instances, the general average being very close to a consumption ratio of 2. This means that surface combustion broiling can be done with about half the gas now required on the Bunsen burner type with feeble radiation and less than half on others. The quality of the work done is uniformly better though it must be confessed that opinion differs somewhat here, never going so far, however, as to charge the surface combustion broiler with inferior work. The intense radiant heat which, of course, is under control, permits the thing being cooked to

be placed from 6 inches to 10 inches away from the burner, promptly sears the outside, prevents the escape of flavoring juices and makes the side that is cooking not only clearly visible but illuminates it so well that the operation can be perfectly carried on in a dark room.

This gas saving of 50 per cent or better for radiant operations like the broiling reported above, is confirmed almost identically by the tests on the radiant room heater, also compared with the Vulcan which carries a perforated cast iron plate attaining a dull to bright red by the heat of a Bunsen bar burner below. Heat was here measured by the temperature rise of a measured body of water in a flat sheet metal box placed in front, far enough away to escape contact with any hot gases. The consumption for equal amounts of heat thus thrown out is almost exactly twice for the Bunsen compared with the surface combustion.

It may be said, therefore, that surface combustion domestic appliances can save in all directly radiant operations about half the gas required by Bunsen appliances and in other cases like top burners and ovens an average of about 35 per cent in round numbers derived from actual tests in laboratory and kitchen. These figures are for continuous operation and are reduced in some cases by intermittent work such as involves the lighting of a burner for a few minutes and then turning it out almost as soon as it gets warm. For such service as this, efficiency is not so important as a quick heat and if less time than one minute be available one present type burner can be retained in each stove for it, reserving for the surface combustion burners the large gas consumption work where gas savings are equivalent to appreciable sums of money.

INSTALLATION OF NEW APPARATUS

At this point the question naturally arises as to when the saving of gas becomes large enough to pay for the electric current consumed by the fan and in what time the net saving will pay for the increased cost of surface combustion appliances over Bunsen. The answer to the last question is to be found only when it is known how much the appliance will be used as the fixed charges per hour of use depend on the number of service hours per year; in this respect the case is similar to plant operation. If a domestic range is to be used one week per year it matters little how efficient it may be and the cheapest thing available in first cost is the thing to buy. On the other hand it will take a very short time to pay for the extra cost of an appliance that is used every day and doubly so if operated many hours per day, especially if the service requires considerable gas. Calculations could be given for all sorts of hypothetical cases but as any one can make them for conditions that are important to him they are here omitted; however, one case is included for illustration.

Suppose a domestic range with a full capacity consumption of 100 cu. ft. per hour were operated three hours per day and three hundred days or 900 operating hours per year at an average rate of 50 cu. ft. per hour with such distribution of various burner service as

corresponds to an average saving of 40 per cent of what a corresponding Bunsen range would require. It may also be assumed that the latter would cost the consumer \$35 and the former \$50 and that gas costs \$1.00 per 1000 cu. ft. and electric current 10 cents per K. W. hour. The surface combustion range would consume per year $50 \times 3 \times 300 = 45,000$ cu. ft. of gas, while the corresponding Bunsen would consume $45,000 \div (1.0 - 0.4) = 75,000$ cu. ft. so that the saving of the former over the latter is 30,000 cu. ft., worth \$30 per year. From this is to be subtracted the cost of 900 hours of electrical supply, which must be estimated. This can be calculated from the power charts given, and it will be found that for even low efficiencies of fan and motor not over 0.5 ampere at 110 volts or 55 watts should be ample. In fact actual measurement of the Regina vacuum cleaner set, illustrated on the first range, Figs. 48 and 49, which had a delivery pressure twice and an air volume about four times what was required, required 92 watts with all burners in operation and 90 with none, proving the excess capacity and the probability of operating with fans and motors designed for the service on less than half an ampere.

Assuming that at the start no efficient fan and motor be available and that the absurdly high consumption of 90 watts would be required for the necessary 10 cu. ft. of air per minute at 4-5 inches water pressure, the electrical cost of operation would be $10 \times 90/1000 = 0.1$ cent per hour, in round numbers, or \$9.00 per year. This makes the net saving in operation \$30.00 — \$9.00 = \$21.00 per year, and as the excess of first cost was assumed to be \$15.00 it would be paid off completely in 600 hours of operation, or if uniformly distributed in $8\frac{1}{2}$ months.

One short way of disposing of the electrical cost is to consider that the gas saved by a single top burner

GAS SAVING NECESSARY TO JUST PAY COST OF ELECTRIC CURRENT EXPENDED FOR FAN OPERATING SURFACE COMBUSTION APPLIANCES

Electric H.P. required by fan	Equivalents watts	Equivalent Amperes at		Current at 10 c. per K. W. hour	rent at \$1.00 per 1000 cu. ft. gas
		110 volts	220 volts		
0.01	7.46	0.06782	0.03391	0.0746	0.75
0.02	14.92	0.13564	0.06782	0.1492	1.49
0.03	22.38	0.20346	0.10173	0.2238	2.24
0.04	29.84	0.27128	0.13564	0.2984	2.98
0.05	37.30	0.33910	0.16955	0.3730	3.73
0.06	44.76	0.40692	0.20346	0.4476	4.48
0.07	52.22	0.47474	0.23737	0.5222	5.22
0.08	59.68	0.54256	0.27128	0.5968	5.97
0.09	67.14	0.61038	0.30519	0.6714	6.71
0.10	74.60	0.67820	0.33910	0.7460	7.46
0.11	82.06	0.74602	0.37301	0.8206	8.21
0.12	89.52	0.81384	0.40692	0.8952	8.95
0.13	96.98	0.88166	0.44083	0.9698	9.70
0.14	104.44	0.94948	0.47474	1.044	10.44

Cu. ft. gas
per hr. cost-
ing same as
electric cur-
rent

will more than pay for the electric current to operate the entire range so that for all burners in operation in excess of one the electrical current costs nothing. That this statement is justified is indicated by the following, assuming the inefficient fan and motor to be used that costs 0.1 cent per hour to operate. If the service of a standard 15 cu. ft. Bunsen top burner

is preferred by a 10 ft. surface combustion burner (ratio 1.5) the gas saving is 5 cu. ft. per hour, which is worth $5 \times 1000/100 = 0.5$ cent per hour, a net saving of 0.4 cent per hour. This shows how conservative is the general estimate above, that other gas saving at one burner will more than defray the expense for current for the entire range, for under the conditions named the gas saving at one burner is five times the cost of current for all of them.

In the preceding table there is given a series of equivalents in gas saving, cu. ft. per hour, the value of which just balances various values of electrical horse power requirements of fan.

CONCLUSION

It is hoped that this review of the development of surface combustion will show that it is now possible to design rather than merely invent apparatus, and that such apparatus as commercial conditions may require may now be produced in no more time than is necessary to decide on the models to be manufactured and the production of an initial stock. However, there is no intention of leaving the impression that the work of development is finished for it is only just fairly started, and should be continued with corresponding improvement in appliances for the next half century.

COLUMBIA UNIVERSITY,
NEW YORK

METHODS FOR THE EXAMINATION OF NATURAL GAS FOR THE PRODUCTION OF GASOLINE

By E. S. MERRIAM AND J. A. BIRCHBY

Received July 18, 1913

The production of natural gas gasoline from the casing head gas of the oil fields, by compression and cooling, has, within the last five years, grown to be a very important industry. Through the failure of many plants to obtain gasoline in paying quantities, it was early recognized that a preliminary examination of any proposed gas should always be made, and naturally the problem was put up to the analytical chemist. Any one at all familiar with the literature on natural gas will realize that positive statements in regard to the presence and quantities of the higher paraffines occurring in natural gas are not numerous. Ethane, propane, and butane were early found in natural gas, but no reliable figures could be given as to their amounts. In fact from combustion data alone only the total quantity of paraffin vapors present can be determined, and not which ones.¹ Generally the results are recorded on the assumption that methane and ethane alone are present.

The exact analysis of a mixture of five hydrocarbon gases does not seem possible, with the means available in an ordinary laboratory. Fractional distillation at -190° C. and -120° C. seems to have given Lebeau and Damiens² good results. The use of high pressures in connection with the critical temperature of the vapors believed to be present might lead to a more or less correct result, though the solubility of a gas in a liquid hydrocarbon must be taken into account.

¹ G. A. Burrell, Bur. of Mines, Bull. 15, 67.

² Compl. rend., 156, 144-7 and 325-7; Chem. Abstracts, 7, 1338.

Even if we had methods whereby the percentage of butanes and pentanes could be determined in a given gas, it would still be a difficult matter to calculate how much of each could be condensed to liquid at any given temperature and pressure, and when it is found that the various makes of compressors and condensers are not equally efficient, it can readily be seen that the chemist should be extremely conservative and cautious in his reports.

In view of these facts it is evident that the most logical method to pursue is to obtain gases from plants where the production is known, and to examine these gases by methods which will respond to the presence of the more readily condensible hydrocarbons. In this way empirical relations between certain physical and chemical properties of the gases and the yields in actual practice can be established, and a probable yield for any unknown gas can be predicted.

A second method is to construct a small compressor so that any gas may be subjected to any desired pressure or any degree of cooling. We have proceeded along both these lines, and the object of this article is to describe the methods which we have found most suitable.

It may be of interest to describe first some methods which we tried and discarded.

First.—By passing the gas through absolute alcohol it was believed that the heavier hydrocarbons would be partially dissolved. If this alcohol be then diluted with water, the hydrocarbons, being insoluble in and lighter than water, would separate and their volume could be determined. This method was used by Bun-

the method did not seem to respond with sufficient delicacy to the presence of the heavier hydrocarbons.

The first method which showed promise was to determine the solubility of the gas in absolute alcohol.¹ The following solubilities are given in Watts' dictionary:

1 volume of alcohol dissolves	0.523 vol. CH ₄ at 0° C.
1 volume of alcohol dissolves	1.5 vols. C ₂ H ₆ .
1 volume of alcohol dissolves	6.0 vols. C ₃ H ₈ .
1 volume of alcohol dissolves	18.0 vols. C ₄ H ₁₀ .

The process used was simply that of Hempel for determining benzene vapors in illuminating gas: 1 cc. of absolute alcohol was placed in a Hempel explosion pipette over mercury, 100 cc. of gas introduced and the decrease in volume noted after three minutes shaking. This decrease will be due to a slight extent to methane, and in an increasingly greater measure to ethane, propane, etc. The 1 cc. of alcohol will be completely saturated with CH₄, probably nearly saturated with C₂H₆, but will in general not be saturated with the heavier constituents which are present in smaller amounts and which have a far higher solubility. If, then, a second quantity of 100 cc. of fresh gas is shaken with this same 1 cc. of alcohol, the decrease in volume this time will be due mainly to the heavier vapors present. Since alcohol has an appreciable vapor tension, is also an oxygen-containing body, and should therefore be a poorer solvent for hydrocarbons than another hydrocarbon, we soon discarded its use and used 1 cc. of kerosene instead. The results obtained by the use of kerosene have proven of great value.

TABLE I

No.	Per cent		D'	A	B	Olive oil			YIELD	PRESSURE	REMARKS
	D	air				A/B	absorption	M			
26	1.305	25.0	1.406	13.6	6.0	2.27	15.8	67	5.0	80	"Gas pump gas"
27	1.276	38.5	1.383	11.1	5.4	2.06	13.2	66	5.0	90	"Gas pump gas"
30	1.41	0.0	...	19.0	6.8	2.79	26.2	65	8.0	80	"Gas pump gas"
33a	1.24	44.0	1.429	11.2	5.7	1.97	14.5	60	5.0	80	"Gas pump gas"
33b	1.12	6.6	1.9	3.48	9.2	58	33a after compression
77	1.244	0.0	...	12.9	4.3	3.0	19.0	58	4.0	...	Taken from well under 50 lbs. pressure
80	1.202	61.0	1.515	6.8	3.2	2.12	8.8	69	Yield 6 to 7 after eliminating air at 225 lbs.
84	1.004	34.0	1.005	2.4	1.1	2.18	5.2	73	0.75	100	
85	0.931	27.5	0.905	3.7	0.4	9.2	4.7	48	0.0	250	This gas had been through a plant at 250 lbs.
96	0.799	0.0	...	4.0	1.1	3.63	5.8	58	0.50	250	Unsuccessful plant
99	0.795	0.0	...	3.4	1.1	3.1	4.7	69	0.25	200	Unsuccessful plant
117	1.087	0.0	...	6.9	1.4	4.92	10.6	52	0.0	180	Gas had been through at 180 lbs.
125	1.398	26.5	1.542	16.0	7.1	2.25	21.4	60	5.0	110	
135	1.31	0.0	...	14.0	4.4	3.18	16.8	57.5	4.0	not known	
136	1.142	17.0	1.171	8.8	2.9	3.04	9.0	61	2.5	...	

sen in showing the presence of benzene in illuminating gas (Hempel-Dennis, "Gas Analysis"). In the case of natural gas, however, owing to the rapid escape of the lighter constituents, such brisk effervescence occurred on diluting that the heavier hydrocarbons were carried off. Even with ice water and in a closed vessel no reliable results could be obtained.

Second.—By treating the gas with a suitable high boiling oil, such as lubricating oil, to absorb the vapors, and then distilling the mixture, it was sought to regain the vapors. The hydrocarbons thus obtained could not be condensed satisfactorily.

Third.—By combustion. This method as mentioned above gives the total paraffins only, and while a rich gas can easily be distinguished from a poor one,

In Table I, the figures under A denote the number of cc. of gas absorbed by 1 cc. of kerosene, under B the absorption when a second 100 cc. of gas is shaken with the same 1 cc. of kerosene. B is, of course, in every case, smaller than A, and is proportional to the heavier constituents present. We have found that the value of B approximately represents the yield of gasoline in gallons per 1000 cu. ft. of gas. When B is small it will exceed the yield; when high it will fall below the yield. The ratio of A to B is also of significance, as can be expected from general principles. If the hydrocarbons causing B are of high molecular weight they should be more readily condensible and show a higher solubility. The first 100 cc. of gas

¹ C. A. Burrell, loc. cit.

therefore will not come so near to saturating the 1 cc. of kerosene, and B will be greater than would be the case if more volatile constituents were present. The ratio of A to B should show something about the condensibility of the vapors and the pressure needed to liquefy them. The determination of A and B should, of course, be made at a fixed temperature; the figures given refer to 20° C.

Further information in regard to the nature of the hydrocarbons can be gained very simply. It is easy to determine the mean molecular weight of the vapors which have dissolved in any solvent. All we need to know is their volume and weight under the temperature and pressure prevailing. For this determination we have used a small vessel of the shape shown in Fig. 1.

This contains some glass beads to increase the surface, and is charged with 5 cc. of olive oil. We have used olive oil rather than a mineral oil since it has practically an unvarying constitution, is non-volatile and does not foam. The olive oil is first saturated with our city gas, which, from combustion data, ap-

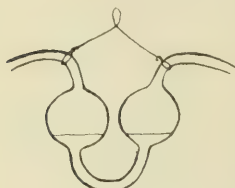


FIG. 1

pears to consist of about 75 per cent methane and 25 per cent ethane; the gas in the upper part of the bulbs is driven out by aspirating through a small amount of air, and the whole is weighed. The bulbs are then connected between a gas burette and Hempel pipette filled with water, and 100 cc. of gas are slowly passed back and forth a dozen times or more, or until no further gas is absorbed. The decrease in volume is noted and the increase in weight of the absorption bulbs. Readings of the temperature (which we have always kept as near 20° C. as possible) and pressure then give all the necessary data for computing the molecular weight of that part of the vapor which has dissolved in the oil.

An example will make the method of calculation clear. In gas No. 26 of Table I, 15.8 cc. of gas were dissolved by the olive oil, and the oil thereby gained in weight 42.9 mg. The temperature was 20° C., and the barometric pressure (corrected for the vapor tension of water) was 740 mm. At 0° and 760 mm. the 15.8 cc. reduces to 14.32 cc. The weight in milligrams of 22.4 cc. of any gas measured at 0° and 760 mm. is equal to the molecular weight M. Therefore, $14.32 : 42.9 = 22.4 : M$. M is 67 in this case. The molecular weight of butane C_4H_{10} is 58, and of pentane C_5H_{12} is 72. It seems certain, therefore, that this gas contains at least 15.8 per cent of condensible hydrocarbons corresponding to butane and pentane. The absorption is, of course, by no means quantitative. It will vary for one thing with the amount of olive oil used. Using mixtures of air and gasoline vapors of known composition we have found it possible, using 5 cc. of oil, to recover from 40 to 60 per cent of the vapor present, according to the volatility of the gasoline used in preparing the mixture.

In any case the figure thus obtained for the molecular

weight of the condensible vapor is of value. From it we can draw conclusions as to the pressure needed and as to the quality of the gasoline obtainable. A low molecular weight would mean a very lively condensate; a high figure would indicate a less volatile gasoline. As a rule the ratio of A to B is also consistent with the molecular-weight determination, a high M going with a low ratio. The determination of M also enables one to tell whether a gas has been subjected to pressure.

These few simple determinations together with the density of the gas and determination of the air present, when checked upon gases where the production is known, enable one to draw a fair conclusion as to the probable yield of any gas.

In Table I are given the results of examination of gases from a number of plants. D gives the density of the gas, taking air as unity. When air is present, the density of the gas itself, D', can be calculated from the formula:

$$D' = \frac{100D - \% \text{ air}}{100 - \% \text{ air}}$$

Under yield is given the number of gallons of gasoline which the operators claim to be making per 1000 cu. ft. of gas. Nos. 26, 27, 30 and 33a are all "gas pump

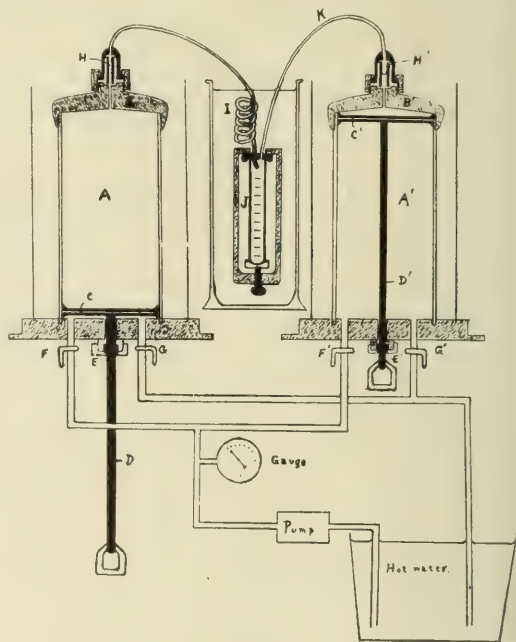


FIG. 2

gas," *i. e.*, are obtained from the wells by use of a vacuum. This process favors the evaporation of the lighter constituents from the oil, and usually gives a rich gas requiring only moderate pressures: 33b is the same gas as 33a after it has been through the plant at 80 lbs. pressure. The change in the figures for A and B and their ratio is quite marked. No. 84 is from a plant which is barely making expenses. No. 85 is gas which has been through a plant at 250 lbs.

pressure. M is extremely low and A/B very high. No. 117 is gas which has been through at 180 lbs. Nos. 96 and 99 are from unsuccessful plants. No. 80 was examined by us and we reported a probable yield of $2\frac{1}{2}$ gals., but stated that if the entrance of air could be avoided a yield of 6 gals. might be expected. The operator went over his lines finding numerous leaks which he repaired, and is now making 6 to 7 gals. per 1000 cu. ft.

For further tests we have constructed a small compressor by which the exact yield under any working conditions can be obtained. The results obtained in this way are free from any uncertainty, and the approximations of the analytical methods and personal equation of the analyst are done away with.

In the accompanying Fig. 2, A and A' are 2 cylinders of polished brass tubing $4" \times 10"$, each fitted with a bronze cap B, B', screwed and soldered on. Each cylinder is provided with a piston C, C', with close fitting leather cups above and below, and a piston rod, D, D', provided with a stuffing box, E, E'. Each cylinder is provided with a water jacket which can be

into the cylinders on top of the pistons; the pistons are then forced up to the top of the cylinders. The excess water is thus forced out, and only enough remains to fill the space between the pistons and caps of the cylinders. Connection is now made with the gas to be tested. By opening the valves G, G' and pressing on the stirrups the pistons are drawn down, and the cylinders filled with a measured volume of gas. The graduated glass tube J is now attached and it and the condenser I are surrounded by the cooling water. Boiling water is placed in the jackets, the valves G, G' closed, and hot water is pumped into cylinder A' through F', forcing the piston up and driving the gas over into A. The rise of the water into the tube H' shows when the gas is all out. The valve F' is now closed. All the gas is now in A. The valve G is closed and hot water is pumped into A, compressing the gas. The gauge shows the pressure. When the desired pressure is obtained, the valve G' is opened very carefully, allowing the right-hand piston to descend. The pump is now operated and the pressure kept constant. The gas thus passes slowly

TABLE II

No.	D	Per cent air	D'	A	B	A/B	Olive oil absorption	M	Empirical formula from combustion data	Calculated D	Yield	Pressure Lbs.	Cooling temperature
145	0.94	0.0	...	7.3	2.5	2.92	8.8	69.0	$C_{1.66}H_{2.59}$	0.88	1.35 2.26 2.94	100 200 250	7° C.
146	1.062	7.0	1.068	8.5	3.2	2.66	10.4	63.5	$C_{1.99}H_{3.10}$	1.045	1.49 2.76 3.58	100 200 300	8° C.
147	0.957	0.0	...	6.6	2.3	2.87	7.9	68.0	$C_{1.91}H_{3.11}$	0.947	1.33 2.34 3.00	100 200 300	7° C.
148	0.802	0.0	...	3.6	0.7	5.15	4.2	105?	$C_{1.49}H_{2.31}$	0.803	0.36 0.64 0.91	100 200 300	15° C.
149	0.958	0.0	...	5.9	2.2	2.68	6.5	76.0	$C_{1.81}H_{3.17}$	0.955	1.43 2.45 3.12	100 250 350	8° C.
161	0.886	0.0	...	5.8	1.6	3.62	6.9	69.0	0.79 0.99 1.26 1.52	100 150 200 300	15° C.

filled with hot water. In the base of the cylinders are two openings, F, F' and G, G', which serve for the entrance and exit of the hot water used for exerting the pressure. By the use of a small boiler testing pump any pressure up to 500 lbs. can be exerted on the gas, and the pressure can be controlled accurately by the gauge which is placed between the pump and cylinders. A nut and sleeve press the small glass tube H, H' into a gas-tight connection on the cap of each cylinder. The sleeve is partially cut away so that the glass tube can be observed. From cylinder A leads a small capillary copper tube, the lower part of which is wound spirally and serves as the condenser I. This passes through a small brass disk against which is pressed a graduated glass tube, J, which serves to collect the condensed liquid. This glass tube is seated tightly with a rubber washer, as are also the tubes H and H'. Through this brass disk passes another tube, K, which conducts the spent gas to the other cylinder. The tube J and condenser I are set in a jar of water of any desired temperature.

The method of operation is as follows: the graduated glass tube J is removed and a little water is drawn

at the desired pressure through the condenser at the desired temperature, and any liquid forming in the condenser is carried down and collects in the glass tube, which is graduated so as to read directly in gallons per 1000 cu. ft. of gas.

The spent gas passes over into cylinder A'. After the gas has passed through at any pressure it can be transferred back by opening G and pumping in at F', and put through again at a higher pressure. As many readings can be made as desired. The use of hot water in the jackets and pump prevents the condensation of gasoline in the cylinders, though it is always advisable, especially in the case of rich gases, to increase the pressure by easy stages. If the pressure were raised to 200 lbs. at the start some liquid might condense in the cylinders and not get over into the measuring tube.

We have found that all the gasoline obtainable at any pressure is thrown down by one operation, a second trip through at the same pressure not yielding any more liquid.

We have found this apparatus to work very well, and have examined a good many samples of gas by the

absorption methods and the compression method.

The results of a few of these tests are given in Table II. Under yield is given the quantity of liquid condensed by use of the compressor described above. This figure is to be looked upon as an upper limit. The yield on the large scale will be less than the figure given, owing to leakage, evaporation losses, imperfect cooling, etc. The combustions were made over mercury, using oxygen and a heated platinum spiral. In almost every case the figure for hydrogen is slightly greater than that corresponding to a paraffin of the formula C_nH_{2n+2} . This is undoubtedly due to experimental error, as it is well established that natural gas does not contain free hydrogen. The density of the gas calculated from the empirical formula agrees fairly well with the observed D.

SUMMARY

I. A few simple empirical tests are given whereby the approximate quantity of gasoline obtainable from natural gas can be determined.

II. A small testing compressor is described.

III. Some typical analyses and tests are given.

MARIETTA COLLEGE
MARIETTA, O.

THE CHEMISTRY OF ANAESTHETICS, V.: ETHYL CHLORIDE¹

By CHARLES BASKERVILLE AND W. A. HAMOR

CHEMICAL HISTORY

Ethyl chloride ("sweet spirit of salt;" *aethylum chloratum*; *aethylis chloridum*; *aether chloratus*; *aether hydrochloricus seu muriaticus*; "hydrochloric ether;" chlorhydric ether; chloro-ethane; mono-chlorethane; chlorethyl; *chloräthyl*; *chlorwasserstoffäther*; *leichter salzäther*; *chlorure d'éthyle*; *ether chlorhydrique*; "chelen" or "chelene;" "kelen" or "kelene;" "anodynone;" "antidolorin;" "ethylol;" "loco-dolor;" etc.) was first obtained in alcoholic solution by Basil Valentine (*pseudo*).² "Sweet Spirit of Salt" was well known to the later chemists. Glauber, for example, referred to it in 1648.

Ludolf stated, in 1749,³ that on heating alcohol with sulfuric acid and sodium chloride, a distillate was obtained which, when treated with lime, yielded an "ether;" but he endeavored in vain to obtain a similar compound by the action of hydrogen chloride ("muri-

atic gas") on alcohol. Baumé was also unsuccessful in this direction, but Woulfe⁴ obtained the preparation in this way, and it was afterwards prepared and sold by an apothecary in Germany under the name of "Basse's hydrochloric ether" (1801).

HISTORY OF ITS USE AS AN ANAESTHETIC

Flourens⁵ drew attention to the anaesthetic properties of ethyl chloride in 1847, and Heyfelder, in the following year, first administered the vapor for surgical purposes. Unsatisfactory symptoms often accompanied its administration at that time, these effects being attributed to imperfections in the manufacture and the consequent presence of impurities. The use of the agent as a general anaesthetic was abandoned until 1895, since which time it has rapidly gained in favor. This is principally attributable to the improved methods of administration, and to an increase in the knowledge of its properties and physiological action; and last, but not least, to improvements in its manufacture.⁶

Ethyl chloride may be regarded as ethyl alcohol (CH_3CH_2OH), in which the OH has been replaced by Cl, hence the formula CH_3CH_2Cl , which was established by Colin and Robiquet.⁴

"Alcoholic (or 'alcoholized') muriatic ether" is a solution of ethyl chloride in an equal amount of alcohol by volume. It has been used as an internal stimulant in doses of 0.6 to 1.8 cc.

USES

So far ethyl chloride has not been used technically, although Palmer⁸ called attention to its advantages (and disadvantages) as an industrial refrigerating agent. In medicine it is used for (a) general anaesthesia (by inhalation); (b) local anaesthesia (by external application, in effect refrigeration); and (c) diagnostic and therapeutic purposes.

PREPARATION

As noted, ethyl chloride may be regarded as ethyl alcohol (C_2H_5OH), in which the hydroxyl has been replaced by chlorine. Ethyl alcohol is the raw product from which it is usually made, although ethyl chloride results in the regulated chlorination of ethane,⁹ on treating acetic and other ethers with hydrogen chloride, by the action of hydrochloric acid on ether in sealed tubes,⁷ and by the action of chlorine on ethyl iodide. In actual practice, ethyl alcohol is mixed

¹ Read at the regular June meeting of the New York Section of the American Chemical Society, 1913.

² He described its preparation thus ("Wiederholung des grossen Steins der uralten Weisen," ed. Petrus, p. 72): "This I also say that, when the spirit of common salt unites with spirit of wine, and is distilled three times, it becomes sweet and loses its sharpness." In his *Last Testament* ("Basilii Valentini," ed. Petrus, p. 786) he also says: "Take of good spirit of salt which has been well dephlegmated and contains no watery particles, one part; pour to this, half a part of the best and most concentrated *spiritus vini* which also contains no phlegma or vegetable mercury." Valentinus goes on to state that this mixture must be repeatedly distilled, and then "placed in a well-closed bottle and allowed to stand for a month or until it has all become quite sweet and has lost its acid taste. Thus is the *spiritus salis et vini* prepared and may be readily extracted."

In 1739, Johann Pott demonstrated that "sweet spirit of salt" could be obtained by the action of "butter of arsenic" or "butter of antimony" (arsenic or antimony trichloride) on spirit of wine, and other chemists found that other metallic chlorides might be employed for the same purpose. Rouelle, in 1759, found that ethyl chloride resulted from the action of sulfur chloride, phosphorus pentachloride, aluminum chloride, ferric chloride, stannic chloride, etc., on alcohol.

³ *Die in der Medicin siegende Chemie*,, Erfurt, 1746-49.

⁴ *Phil. Trans.*, 1767, 520.

⁵ Hewitt, "Anaesthetics," 1907, 11.

⁶ In 1880, a committee of the British Medical Society reported that ethyl chloride was not safe to employ as a general anaesthetic, owing to its liability to produce respiratory failure and convulsions. In 1898, it was stated in Sajous' *Annual*: "We would also warn against its (ethyl chloride) use for the purpose of inducing general anaesthesia, as the dangers incurred therefrom are too great." Interest in its use was revived in the same year, however, by the reports of Lotheisen, and in 1901 by McCardie, who cited a large number of successful cases in general anaesthesia. To quote Dodge [*Boston Med. Surg. J.*, 1909, 234 (February 25)]: "It is believed that the bad results obtained earlier were due partly to impure preparation of the drug, as well as improper methods of administration."

Ware (*J. Am. Med. Assn.*, November 8, 1902) directed attention to the fact that preparations marketed in this country in 1902 contained methyl chloride to facilitate evaporation.

⁷ *Ann. chim. phys.*, [2], 1, 343.

⁸ *Eng. Digest*, 5, 262.

⁹ *Darling, Ann.*, 150, 216; Schorlemmer, *Compt. rend.*, 58, 703.

⁷ Berthelot.

with hydrogen chloride, which acts as a desiccating agent itself,¹ or dehydrating agents, as zinc chloride² or phosphorus pentoxide,³ are added to remove the water produced. If these agents were not added, the reversible reaction would reach an equilibrium. This equilibrium may be avoided by increase of pressure.⁴ It is also manufactured by mixing concentrated sulfuric acid (2 parts) with 96 per cent. alcohol (1 part), and, after standing, diluting with water (1/2 part), adding potassium chloride, and distilling.

IMPURITIES FROM MATERIALS USED

If pure hydrogen chloride is used, there is little danger of impurities being introduced from that source. The quality of the alcohol used, however, is very important. If denatured alcohol, especially if wood alcohol be the denaturant or one of the denaturing substances,⁵ then methyl chloride will likely be produced. This gas (b. p. $-23.7^{\circ}\text{C}.$), while very soluble in ethyl chloride, may easily be removed by rectification. Aldehydes form compounds with hydrogen chloride. Any acetic acid present is liable to form acetyl chloride, and the higher alcohols, as propyl, butyl and amyl, produce their corresponding halogen derivatives. It is desirable, therefore, to use only absolute alcohol of the highest degree of rectification.

An examination of seven different makes of ethyl chloride obtainable in London in 1905 showed that all the branded samples were pure, as was also one unbranded sample. The report of this investigation⁶ states that ethyl chloride should be free from water, foreign chlorides, acids, aldehydes, ether, alcohol, and organo-metallic substances.

¹ Ethyl chloride may be prepared by distilling ethyl alcohol (5 parts), sulfuric acid (2 parts) and sodium chloride (12 parts) together, or by passing dry hydrogen chloride into absolute alcohol; but it is said that the action of hydrochloric acid upon alcohol gives a poor yield of chloride unless zinc chloride is added to the alcohol before passing in hydrochloric acid [Groves, *J. Chem. Soc.*, **27**, 637 (1874)]. Groves found that when hydrochloric acid gas was passed into a boiling solution of zinc chloride (2 parts) in 95 per cent. ethyl alcohol (3 parts), the yield was nearly theoretical. He purified the product by washing with water.

² Kruger (*J. prakt. Chem.*, [2], **14**, 193) recommended that a mixture of one part of zinc chloride in 82 parts of ethyl alcohol should be saturated with hydrochloric acid gas in the cold and then heated to the boiling point. Hydrochloric acid gas being conducted into the mixture during distillation, as the process is carried out, a reflux condenser prevents the alcohol vapor from coming over and the zinc chloride is said to act by abstracting water from the alcohol, the nascent ethylene combining with hydrogen chloride to form ethyl chloride, according to Schorlemmer (*J. Chem. Soc.*, **1875**, 308). On the action of hydrochloric acid on alcohol, alone and in the presence of zinc chloride, see also Ribouquet and Colin, *Ann. chim. phys.*, [2], **1**, 343; Regnault, *Ibid.*, [2], **71**, 355; Kuhlmann, *Ann.*, **33**, 108; and Lowig, *Pogg. Ann.*, **45**, 346. On velocity of the reaction, see Kailan, *Monatsh.*, **28**, 559 (1907). The formation of ethyl chloride in this process is partly due to the action of hydrogen chloride upon alcohol and partly to the union of this nascent ethylene with hydrogen chloride.

³ The practice of some American manufacturers is to use phosphorus pentoxide as the dehydrating agent.

⁴ The process of Mennet and Cartier (French Patent 206,574, June 23, 1890) relates to the production of ethyl chloride. An autoclave of 150 liters capacity is used, into which a mixture of 95 kg. of hydrochloric acid (21°Be.) and 34 kg. of 93-95 per cent. ethyl alcohol is maintained at 50 atmospheres pressure and at 130°C. for about 28 hours. The pressure is then diminished to 42 atmospheres and finally the autoclave is cooled. See also Hager's "*Handbuch d. Pharm. Praxis*," **1**, 189 (1910).

⁵ The Commissioner of Internal Revenue ruled in 1907 that the use of alcohol would be allowed tax free in the manufacture of ethyl chloride in accordance with Section 40, Part VI, of the revised regulations, after September 1, 1907, provided the finished product contained no alcohol. The following formula was authorized for use in the manufacture of ethyl chloride: To 100 gallons of ethyl alcohol add 5 gallons of approved wood alcohol.

⁶ *Lancet*, **1905**, ii, 1651

PURIFICATION

Ethyl chloride is purified¹ by passing the vapor through water, dilute caustic solution and then concentrated sulfuric acid. The treatment is intended to free it from alcohol,² hydrogen chloride,³ and water. Re-distillation is sometimes practised. This rectification serves to remove other alkyl chlorides, the methyl going off in the first fractions of the distillate and the higher compounds remaining in the residue.

PROPERTIES

Ethyl chloride is a colorless mobile liquid at low temperatures and is extremely volatile. It possesses a slightly saccharine taste and a penetrating and pungent, yet fragrant, "ethereal" odor. It is inflammable, burning, when ignited, with a smoky green-edged flame, producing fumes of hydrogen chloride; hence, care must be exercised in using it near an open flame or a hot cautery. It decomposes even when very close to a hot bulb or an incandescent electric light.

Ethyl chloride has a melting point of -142.5°C. ; it possesses a boiling point of $+12.5^{\circ}\text{C.}$; and its specific gravity is 0.92138 at 0° ,⁴ 0.9176 at $+8^{\circ}$,⁵ 0.8510 at $+12^{\circ}$,⁷ and at $+25^{\circ}$ ⁸ the vapor has a specific gravity of 0.91708. Its vapor density is 2.22.

Water dissolves about one-fiftieth of its weight of ethyl chloride and acquires a sweetish, ethereal taste. Ethyl chloride is readily soluble in ethyl alcohol and ethyl ether, and neither solution should give a reaction with silver nitrate at ordinary temperatures. Ethyl chloride dissolves phosphorus, sulfur, fats, oils, and many resins. It combines with many metallic chlorides—for example, antimony pentachloride and ferric chloride—to form crystalline compounds. It is decomposed at a red heat into ethylene and hydrogen chloride.

STORAGE AND CONTAINERS

Owing to its extreme volatility, ethyl chloride cannot be kept in ordinary bottles, except at a temperature below $+10^{\circ}\text{C.}$, and even then the stopper must be tight-fitting and very well secured, and the bottles should preferably be stored in an inverted position. Ethyl chloride is now supplied on the market in sealed or mechanically capped glass or metal tubes of convenient forms, wherein the ethyl chloride is held under pressure. Automatic closing tubes are preferable for local anaesthesia, and there are at least five different types of these on the American market, each manufacturer using his special form of container. Ethyl chloride is also furnished by certain manufacturers in plain capped tubes.

Containers of ethyl chloride should be kept in a dark, cool place, remote from lights or fire; and no empty tubes should be refilled with a fresh lot of the compound, since such an economy may result in spreading infection.

¹ *Pharm. J.*, [4], **15**, 694.

² Acetyl chloride decomposes into acetic and hydrochloric acids with water.

³ And other bodies forming acids with water.

⁴ Regnault, *Jahresber.*, **1863**, 67.

⁵ Pierre, *Compt. rend.*, **27**, 213. Darling, *Lancet*, **21**, 3280 found a density of 0.9252 at this temperature.

⁶ Linnemann, *Ann.*, **160**, 198.

⁷ Ramsay, *J. Chem. Soc.*, **35**, 470.

⁸ Perkin, *J. prakt. Chem.*, [2], **31**, 481.

GLASS VS. METAL CONTAINERS

It is maintained by some that ethyl chloride decomposes when exposed to air and sunlight, hence that the drug should be kept in metal containers. It is further claimed that inasmuch as ethyl chloride is inflammable, there is less danger of breaking in accidentally dropping the metal container. In opposition to this, it may be said that in filling any container, no air remains in it on account of the great volatility of ethyl chloride. Furthermore, in drawing off a portion of the contents of a tube, pressure is produced within the tube which is constant for each temperature, it matters not how much liquid ethyl chloride is present, so long as there is some liquid there; hence no backward pressure is created, whereby air may be drawn into the tube. Undoubtedly light facilitates the decomposition of ethyl chloride by oxygen, but the authors have found that light produces no apparent change in pure ethyl chloride when oxygen is absent.¹ Assuming that the ethyl chloride is pure, there is another objection to the use of a metal container, namely,

DETECTION OF IMPURITIES IN ETHYL CHLORIDE

The impurities likely to occur in ethyl chloride are (a) those which it brings with it from the manufacturer, and (b) those resulting through careless storage. While the exact nature of all these is unknown, yet ethyl chloride complying with the requirements of the pharmacopoeias, as given below, is entirely suitable for the purposes for which it is intended. On account of its volatility, the examination of ethyl chloride presents more difficulties than are encountered in the cases of ethyl ether and chloroform; and it is indeed fortunate that it may be easily prepared in a state of comparative chemical purity.

The *Pharmacopoeia of the United States*¹ prescribes the following tests for purity:

1. "If 10 cc. of ethyl chloride, while cold, be dissolved in alcohol, and a few drops of silver nitrate T. S. be added, no turbidity should be produced (*absence of hydrochloric acid*)."
2. "If 10 cc. of ethyl chloride be agitated with 10 cc. of cold water and the supernatant stratum of

TABLE I—THE RESULTS OF AN EXAMINATION OF AMERICAN ETHYL CHLORIDES

Sample	Description	Odor (U. S. P. test): sulfur compounds, etc.	Residue (B. P. test)	Reaction with litmus (B. P. and P. H. tests)	Hydrochloric acid (U. S. P. test)	Metallic chlorides	Alcohol (U. S. P. test)
1.....	"Antidolorin," contained in a nickel-plated tube	No foreign or unpleasant odor	None	Negative	Absent	Absent	Absent
2.....	"Gebauer's Ethyl Chlorid C. P." contained in nickel-plated tube	"	"	"	"	"	"
3.....	"Kelene," contained in a colorless glass tube	"	"	"	"	"	"
4.....	"Ethyl Chloride Squibb," contained in colorless glass tube	"	"	"	"	"	"

inability to tell how much of the preparation is within the tube and how much has been or is being used in the anaesthesia. This has been met by having a graduated (3 cc. capacity) dropper made of glass which may be attached to the metal container.

IMPURITIES WHICH MAY DEVELOP IN ETHYL CHLORIDE

Uncertain results have been encountered by several who have used ethyl chloride for general anaesthesia and these have been attributed in some cases to impurities that were present and have been detected chemically.²

The original product must not have been properly purified, for the conditions essential for the decomposition of ethyl chloride itself involve oxygen, and, as unadvertised, oxygen has no opportunity to enter the receptacles in which ethyl chloride is dispensed. The presence of small amounts of water may bring about a reverse change in ethyl chloride, with the formation of ethyl alcohol and hydrogen chloride. The latter may readily be detected by spraying some of the drug into a clear silver nitrate solution.

¹ Five samples of "Kelene" and "Ethyl Chloride Squibb," both of which were contained in colorless glass tubes, securely capped, as delivered to the trade, were suspended, at room temperature, inside of a window having direct southern exposure for a period of 21 months, at the end of which time no apparent decomposition had occurred. The exposed samples complied in full with the various pharmacopoeial requirements (see *infra*).

Five samples of "Kelene" and "Ethyl Chloride Squibb" were also exposed, under exactly the same conditions, for a period of 8 months, and the results were the same as above. In samples from which varying amounts of ethyl chloride had been withdrawn, no decomposition occurred for the same periods.

² Hawley, *J. Am. Med. Assn.*, **47**, 502 (1906).

ethyl chloride be evaporated spontaneously, and if a few drops of potassium dichromate T. S. be added to the remaining aqueous liquid, followed by some diluted sulfuric acid, and the mixture be boiled, no odor of aldehyde should be developed, and a greenish or purplish color should not be produced in the liquid (*absence of alcohol*)."

3. "On allowing ethyl chloride to evaporate from clean, odorless blotting paper, which has been saturated with it, no unpleasant odor should remain upon the paper (*absence of sulfur compounds, etc.*)."

The *British Pharmacopoeia* requires that it should leave no residue on evaporation and that an aqueous or alcohol extract should have no acid reaction with blue litmus paper. The *Deutsches Arzneibuch*² requires also that "during evaporation, and thereafter, no garlic odor should be apparent (phosphorus compounds)." The *French Codex*,³ while giving the incorrect specific gravity, states that it should be free from ethyl bromide and iodide. The *Pharmacopoeia Helvetica*⁴ requires that when its vapors are led through water, the water must not give an acid reaction with litmus nor a reaction with silver nitrate.

All the pharmacopoeial tests seek to eliminate acids.

In the opinion of the authors, ethyl chloride intended

¹ 8th Decennial Revision, p. 32.

² 1910, p. 37.

³ 1908, p. 249.

⁴ 1907, p. 27.

for anaesthetic purposes should comply with the following requirements:

1. *Boiling Point.* Ethyl chloride should possess a boiling point of $+12.5^{\circ}\text{C}$.

2. *Odor.*—On allowing 30 cc. of ethyl chloride to evaporate from a filter paper $1\frac{1}{2}$ cm. in diameter, no foreign or unpleasant odor, especially a garlic odor (indicating phosphorus compounds), should be apparent either during or subsequent to evaporation.

3. *Residue.*—When 60 cc. of ethyl chloride are allowed to evaporate in a platinum dish at room temperature, there should be left no weighable residue.

4. *Alcohol.*—When 10 cc. of ethyl chloride are agitated with 10 cc. of distilled water, both of which are at about 10°C ., in a glass stoppered tube, and the supernatant layer of ethyl chloride is allowed to evaporate spontaneously from the opened tube at room temperature, and then 3 drops of potassium dichromate T. S. are added to the remaining water, followed by 5 drops of dilute sulfuric acid, and the mixture is then boiled, no odor of acetaldehyde should be apparent and no greenish or bluish color should be produced in the liquid.

5. *Hydrochloric Acid and Metallic Chlorides.*—On dissolving 10 cc. of ethyl chloride in 10 cc. of 95 per cent alcohol U. S. P., and then adding 3 drops of silver nitrate T. S., no turbidity, even faint, should result, and no precipitate should form.

A simple combination test for the purity of ethyl chloride consists in attaching a 30 cc. ethyl chloride container to a glass tube vial containing 35 cc. of water kept at 40°C . A slow stream of ethyl chloride is passed through the water until the container is emptied, and then 10 cc. of the water are tested with litmus paper, to which it should impart no acid reaction; 10 cc. with silver nitrate T. S., as in test 5 above; and 10 cc. are finally tested for alcohol as in test 4 above.

THE PURITY OF THE ETHYL CHLORIDES ON THE AMERICAN MARKET

Recently the authors examined the products of four American manufacturers, in order to ascertain whether the grades in use complied with the requirements of the various pharmacopoeias above cited. The results are presented in Table I. It will be seen that all the samples examined were of official grade. American manufacturers appear to take the necessary simple precautions to guard against the presence of organic impurities.

COLLEGE OF THE CITY OF NEW YORK

A RAPID VOLUMETRIC METHOD FOR DETERMINING *o*-*m*- AND *p*-CRESOLS, THYMOL AND PHENOL

By L. V. REDMAN, A. J. WEITH AND F. P. BROCK

Received July 14, 1913

This method determines by one titration rapidly and accurately:

- Ortho-, meta- and para-cresols or phenol.
- The meta-cresol in the presence of *o*- and *p*-cresol.
- Phenol in the presence of *o*- and *p*-cresol.

D. The meta-cresol, the phenol and the sum of the *o*- and *p*-cresols in any mixture of these compounds.

Three methods have been proposed for determining the cresols separately: (1) gravimetric,¹ weighing the ortho- and para-cresol as the dibrom-cresol-bromide, the meta-cresol as tribrom-cresol-bromide; (2) volumetric,¹ by Koppeschaar's solution, titrating back the unabsorbed bromine; (3) volumetric, by using a solution of iodine² in sodium acetate and titrating back the unabsorbed iodine with thiosulfate. This latter method does not serve for the quantitative determination of *m*-cresol.

A special method has been devised for determining *m*-cresol^{3,4} in the presence of ortho- and para-cresol, by weighing the *m* cresol as trinitro *m* cresol. The *o*- and *p*-cresol are oxidized away by strong nitric acid and trinitro-phenol is soluble if present in small amounts, *i. e.*, up to 10 per cent. The method, therefore, is reliable in the presence of *o*- and *p*-cresol and less than 10 per cent of phenol. H. Ditz⁵ has given the following equations whereby the *m*-cresol present in a mixture consisting only of the three *o*-cresols may be determined

$$x + y = a \quad (1)$$

$$\frac{3\text{Br}.x}{108.064} + \frac{2\text{Br}.y}{108.064} = b \quad (2)$$

x = meta-cresol.

y = *o*- and *p*-cresol.

a = Wt. of mixture of cresols taken.

b = Wt. of Br disappearing.

Br = 79.97 grams.

The same equations will apply to a mixture of the *o*- or *p*-cresols and phenol. The equation (2) is modified for the formula weight of the phenol⁶ as follows:

$$\frac{3\text{Br}.x}{94.048} + \frac{2\text{Br}.y}{108.064} = b \quad (3)$$

x = the amount of phenol in the mixture taken.

Siegfried and Zimmermann⁷ have criticized H. Ditz and Cedivoda's method and have shown that variable results from 2–20 per cent are obtained by brominating the cresols in an acid bromine solution. Their method varies from that of Koppeschaar's for determining phenol, only in the fact that one hour's time is allowed after the KI is added before the thiosulfate is run into the solution. F. Russig and G. Fortmann⁴ have also criticized Ditz and Cedivoda's method adversely. Ditz replied⁸ to their objections and H. Ditz and F. Bardach⁹ have published results at variance with Russig and Fortmann's conclusions.

Recently Pence¹⁰ has shown that Koppeschaar's solution in an acid menstrum will determine quanti-

¹ Ditz and Cedivoda, *Z. angew. Chem.*, **12**, 1873 (1899). Ditz and Bardach, *Biochem. Z.*, **37**, 272 (1911). Siegfried and Zimmermann, *Biochem. Z.*, **29**, 368 (1910).

² Pence, *This Journal*, **4**, 518 (1912).

³ F. Raschig, *Z. angew. Chem.*, **13**, 759 (1900).

⁴ F. Russig and G. Fortmann, *Ibid.*, **14**, 157 (1901).

⁵ H. Ditz, *Ibid.*, **13**, 1050 (1900). H. Ditz and F. Bardach, *Biochem. Z.*, **37**, 272 (1911).

⁶ Siegfried and Zimmermann, *Biochem. Z.*, **29**, 368 (1910).

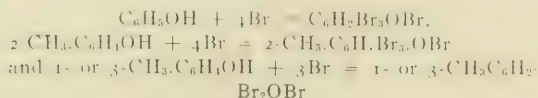
⁷ *Biochem. Z.*, **37**, 272 (1911).

⁸ *Z. angew. Chem.*, **13**, 1050 (1900).

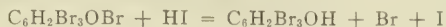
⁹ *Biochem. Z.*, **37**, 272 (1911).

¹⁰ *This Journal*, **4**, 518 (1912).

tatively the meta cresol as tribrom meta cresol. But the ortho and para cresols could not be determined either as the dibrom-cresols or the dibrom-cresol bromide, since the amount of bromine absorbed varied between the amounts required to form the dibrom cresol and the dibrom cresol bromide. Phenol, *o*, *m* and *p*-cresols all form the bromides in the presence of excess bromine, and if the precipitates are filtered off before the KI is added the reaction is nearly quantitative,¹ according to the following equations:



The methyl group of the cresols will be slowly replaced by Br if left in contact with excess Br for several days. This has been shown by Autenrieth and Beuttel.² However, if the KI be added while the precipitate is present in the acid solution the free hydriodic acid reduces the bromide as follows:



This reduction is complete for phenol³ and meta-cresol;⁴ consequently they may be determined accurately by adding bromide bromate to their acid solution, later adding KI and titrating back with thiosulfate. For the *o*- and *p*-cresol the case is somewhat different. The hydriodic acid does not reduce the bromide completely in a reasonable length of time, and as a consequence, all the results of the different investigators show that by this method more than 2 mols of bromine are absorbed for each mol of *o*- or *p*-cresol present. The authors of this paper have brominated the *o*- and *p*-cresols by the same method as described by Koppeschaar and modified⁵ later for determining phenol, and the results have shown in every experiment that the bromine in the hydroxyl is gradually replaced by the hydrogen of the hydriodic acid, but the reaction is so slow that after an hour's time 6 to 40 per cent of the bromine still remains in the hydroxyl. For rapid and accurate work then, the acid bromine menstruum is not satisfactory in determining *o*- and *p*-cresols.

Recently a method was devised by Wilkie,⁶ using a sodium bicarbonate and iodine solution for determining phenol. The authors of this paper have found the method quite accurate and when modified by diluting and continuous shaking¹ the phenol may be determined to an accuracy of two parts in a thousand with a reaction period of only one minute. No subsequent filtering off of the precipitate is needed as in Wilkie's method. The short reaction period does not render the precipitate enough to obscure the end point. Wilkie's method is a modification of Messenger and Vortmann's,⁷ who used caustic soda in place of sodium bicarbonate.

¹ Ditz and Cedivoda, *Z. angew. Chem.*, **12**, 1873 (1899). Autenrieth and Beuttel, *Arch. Pharm.*, **248**, 112 (1910). A. Seidell, *Am. Chem. J.*, **47**, 523 (1912).

² W. Autenrieth and F. Beuttel, *Archiv. der Pharm.*, **248**, 112 (1910).

³ Rhodes and Redman, *This Journal*, **4**, 655 (1912).

⁴ Pence, *This Journal*, **4**, 518 (1912).

⁵ *Ibid.*, **4**, 655 (1912); **5**, 389 (1913).

⁶ Wilkie, *J. S. C. I.*, **30**, 398 (1911).

⁷ Messenger and Vortmann, *Ber. d. chem. Ges.*, **23**, 2753

Messenger and Vortmann's results are not very satisfactory. Gardner¹ and Hodgson have modified Messenger and Vortmann's method so that only one iodine is absorbed by each mol of phenol.

Pence² has used an iodine solution for determining *o*- and *p*-cresol in the presence of sodium acetate. He found that this method would work satisfactorily for *o*- and *p*-cresol but not for the meta cresol. The present authors have found iodine in sodium acetate too slow for a reaction period of one minute. (Pence recommends one hour.)

The authors of this paper have not tested the gravimetric method for determining the cresols as dibrom-*o*- and *p*-cresol bromides and tri-brom-*m*-cresol bromide as the gravimetric is tedious and slow in the drying of the precipitates; the precipitate gives off the odor of bromine during drying and is at best not accurate within 1-2 per cent.³

Problem.—There remains then to discover a rapid and accurate volumetric method, which will serve equally well for the determination of each of the three cresols and phenol. If such a method can be found, it will be possible to determine by a single titration (1) the amount of *m*-cresol in a mixture of the three cresols, (2) the amount of phenol in a mixture of *o*-, *p*-cresol and phenol, (3) the amount of phenol and meta-cresol and the sum of the *o*- and *p*-cresols in a mixture of all four.

The Method.—Such a method has been found by determining the cresols in very dilute⁴ solution, *N*/100, using an *N*/30 solution of iodine⁵ dissolved in KI, adding the sodium bicarbonate⁶ until the mixture is about 1/2 normal, shaking continuously the reacting mixture for one minute, acidifying and titrating back the excess iodine with thiosulfate.

EXPERIMENTAL

Apparatus.—The only appliances needed are (1) standardized burettes, (2) ground stoppered 1/2 liter bottles, (3) 25 and 50 cc. pipettes and a shaking machine. The authors found that continuous shaking by hand of the bottles was as convenient as using the shaking machine when the "reaction period" was of only one minute's duration.

Solutions.—The solutions consisted of *N*/30 iodine, solutions containing 1/60 formula weight of each of the three cresols and phenol, *N*/10 thiosulfate, *N* sodium bicarbonate, 2 *N* sulfuric acid. The *N*/30 iodine was made up by dissolving 4.2 grams of re-sublimed iodine in a saturated solution of 15 grams KI, and making up to 1 liter. The standardization of the iodine solution was by arsenious acid. The thiosulfate solution was prepared by dissolving 125 grams of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in 5 liters of water, allowing the solution to stand for one week and then standardizing it against the iodine.

The three cresol solutions were made up in each case by taking 1.801 grams of redistilled cresol and

¹ W. M. Gardner and H. H. Hodgson, *J. Chem. Soc.*, **95**, 1819 (1909).

² Pence, *This Journal*, **4**, 518 (1912).

³ Siegfried and Zimmermann, *Biochem. Z.*, **29**, 368 (1910).

⁴ Redman and Rhodes, *This Journal*, **4**, 655 (1912).

⁵ Messenger and Vortmann, *Ber.*, **23**, 2753.

⁶ Wilkie, *J. S. C. I.*, **30**, 398 (1911).

making it up to 1 liter. The cresols were from "Merck's highest purity" and were weighed out very carefully after redistilling.

Care was taken to exclude moisture and the samples were weighed out and made up accurately to volume. The *N* sodium bicarbonate solution was made by dissolving 84.1 grams of NaHCO_3 in 1 liter of water, the 2 *N* sulfuric acid by adding 56 cc. of concentrated bottle acid (sp. gr. 1.84) to about $\frac{1}{2}$ liter distilled water, and making the total volume up to one liter. The two latter solutions need be only approximate.

Brominating the Cresols.—At the beginning of the research a bromide-bromate solution was used and acid added as in determining phenol. The bromination method was found to work quite satisfactorily for phenol and meta-cresol, but the amount of bromine absorbed by the *o*- and *p*-cresol at the end of the thiosulfate titration depends upon three factors:

- (1) The excess of free bromine present.
- (2) The length of time the bromine has acted upon the cresol solution.
- (3) The time allowed for the hydriodic acid to act upon the brominated product, reducing the dibrom-cresol bromide to the dibrom-cresol.

If enough bromine be added the reaction is complete and dibrom-cresol bromide is formed and may be weighed as such.¹ But if the reaction in the presence of excess bromine proceeds for only one minute, the reaction is not complete. After allowing the hydriodic acid to reduce it for one minute and titrating back the excess iodine, 6 to 10 per cent of the hydroxyl still remains filled by bromine, giving an error in the determination of 3 to 5 per cent. The longer the hydriodic acid acts upon the product, the less bromine is left in the hydroxyl until after one hour's time the reduction has proceeded within 4 per cent of completion. The difficulty seems to be one of delayed diffusion. The precipitate, which is at first flocculent and fills the whole solution, condenses into a few small, solid wax-like particles which do not allow the hydriodic acid free access to the unreduced bromide. The precipitate which originally occupied a space of $\frac{1}{4}$ liter shrinks (with partial solution) to a volume of less than 1 cubic millimeter, and when the colorless point is reached with the thiosulfate, one can see a continuous column of blue rising from the little granules at the bottom of the liquid, showing that the hydriodic acid is reducing (but very slowly) the dibrom-cresol bromide. Siegfried and Zimmermann² tried to hasten the reduction by warming the solution, but their attempts were unsuccessful. They recommend diluting the solution to 0.025 *N* and allowing 15 minutes for the "reaction period" without continuous shaking, then adding the KI, thoroughly shaking and titrating with thiosulfate. Their results show that the cresols may be determined by this method within 1 to 3 per cent. Our experiments confirmed their results. One difference was observed; if the shaking was continuous, the precipitate decreased in volume as described above and the determination was not accurate.

The bromine-acid method was abandoned in favor of the alkaline iodine method as the results are too dependent upon the dexterity and patience of the individual experimenters. Time was also a factor. The bromine method could not be hastened by shaking as in the case of phenol and meta-cresol, for the precipitates of dibrom-*o*- and *p*-cresol bromide coagulated into such small dimensions that rapid diffusion through it of the hydriodic acid was quite impossible. Allowing a reaction period of fifteen minutes and a reduction period for the bromide of one hour after the KI is added, the method requires about one and one-half hours for determinations which are accurate only to 1 to 3 per cent. When this method is applied to a mixture of phenol and *o*- or *p*-cresol the error is aggravated and amounts to 3 to 21 per cent, according to Siegfried and Zimmermann.¹

DETERMINATION OF *o*-, *m*- AND *p*-CRESOLS SEPARATELY

Each of the cresols was determined separately, according to the following method: About 50 cc. *N* sodium bicarbonate were poured into a $\frac{1}{2}$ liter ground stoppered bottle, 100 cc. of water added, 15 or 20 cc. of the *N*/10 cresol were then run in from a standardized burette, and the volume was very carefully read. Enough *N*/30 iodine (40–70 cc.) to color the solution a permanent alkaline iodine color was then added. A reaction period of 1 minute was allowed, during which time the solution was shaken continuously, by hand or in the machine. Then 50 cc. 2 *N* sulfuric acid were added and after shaking thoroughly the excess iodine was titrated back with thiosulfate.

Tables I, II and III show the results for the three cresols.

TABLE I DETERMINATION OF META-CRESOL

Ex. No.	NaHCO_3 Cc.	Water Cc.	<i>N</i> 10 <i>m</i> -cresol Cc.	<i>N</i> 30 iodine Cc.	Reaction period Min.	2 <i>N</i> acid added Cc.	Thio Cc.	Per cent found of <i>m</i> -cresol
1	20	100	20.00	70	10	25	4.20	100.0
2	20	100	20.00	70	10	25	4.20	100.0
3	20	100	15.00	50	10	25	2.26	100.0
4	30	100	14.97	50	5	20	2.26	99.9
5	50	50	15.02	50	5	30	2.20	100.0
6	100		15.00	50	5	30	2.25	99.8
7	(a)		15.00	50	5	15	3.20	93.4
8	(a)		15.00	50	5	55	3.30	92.7
9	50	100	15.00	50	1	30	2.20	100.2

(a) 100 cc. *N* sodium acetate were added in place of the bicarbonate.

For solutions, etc., see Table III

Experiments 1 and 2 show that 20 per cent excess iodine and 10 minutes' "reaction period" do not increase the absorption of iodine over the 1 minute's reaction and 14 per cent excess free iodine in Experiment 9.

Experiments 3 and 6 show that an increase of sodium bicarbonate from $\frac{1}{6}$ *N* to normal does not increase the iodine absorption.

Sodium acetate was substituted for sodium bicarbonate in Experiments 7 and 8 which confirm Pence's² results that the *m*-cresol does not go over completely to tribrom-*m*-cresol in a short time in the presence of sodium acetate.

¹ Ditz and Cedivoda. *Z. angew. Chem.*, **12**, 1873 (1899).

² Siegfried and Zimmermann, *Biochem. Z.*, **29**, 368 (1910).

¹ Siegfried and Zimmermann, *Biochem. Z.*, **29**, 387 (1910).

Pence, *THIS JOURNAL*, **4**, 518 (1912).

TABLE II. DETERMINATION OF ORTHO-CRESOL.

Ex. No.	NaHCO ₃ Cc.	Water Cc.	N/10 cresol Cc.	N/10 iodine Cc.	Reaction period Min.	2 N acid added Cc.	Thio Cc.	Per cent found of cresol
10	100		15.00	35.0	5	55	1.70	100.0
11	50	50	15.00	39.9	5	30	3.37	99.96
12	50	50	20.03	50.0	1	30	3.33	99.60
13	50	50	20.00	50.0	1	30	3.41	99.90
14	50	50	15.00	40.0	1	30	3.14	100.30

For solutions, etc., see Table III.

Experiments 10 and 11 show that the results are not affected by increasing the excess of free iodine from 11 to 22 per cent and Experiments 12, 13 and 14 show the absorption to be complete in 1 minute's time.

TABLE III. DETERMINATION OF PARA-CRESOL.

Ex. No.	NaHCO ₃ Cc.	Water Cc.	N/10 cresol Cc.	N/10 iodine Cc.	Reaction period Min.	2 N acid added Cc.	Thio Cc.	Per cent found of cresol
15	50	50	20.00	50.3	1	30	3.55	100.7
16	50	50	15.00	50.0	1	30	6.80	100.0
17	50	50	15.00	40.0	1	30	3.29	100.0
18	50	50	15.00	40.0	1	30	3.22	100.0

Thiosulphate = 0.0982 N.

Iodine = 0.0340 N.

Sulphuric acid = 2 N.

Temperature = 23° C.

NaHCO₃ = N.

Experiments 15, 16, 17 and 18 show that uniform results are obtained by making the solution $\frac{1}{2}$ N with sodium bicarbonate, allowing only 1 minute for the "reaction period." Excess of iodine (50 per cent in Experiment 16) did not increase the iodine absorption. It was consequently considered unnecessary to determine the effects of increased "reaction period."

It may be mentioned that the tri-iodo-meta- and di-iodo-para-cresols are precipitated as white flocculent masses before the solution is acidified. The di-iodo-ortho-cresols is precipitated as a red, more or less granular substance. On the other hand, iodo-phenol is not precipitated in $N/2$ sodium bicarbonate and the precipitate forms only on the addition of the acid. In $N/10$ sodium bicarbonate the precipitate forms and is not so red as the precipitate from the stronger carbonate solution.

TABLE IV.—DETERMINATION OF PHENOL BY IODINE-SODIUM-BICARBONATE SOLUTION

Ex. No.	NaHCO ₃ Cc.	Water Cc.	Phenol sol. Cc.	Iodine Cc.	Reaction period Min.	2 N acid added Cc.	Thio Cc.	Per cent found phenol
19	10	90	15	50	1	20	5.00	85.5
20	10	90	15	50	1	25	3.70	94.9
21	10	90	15	50	15	25	3.20	98.6
22	25	75	15	50	1	25	3.00	100.0
23	50	50	15	50	1	30	3.00	100.0
24	50	50	15	50	1	30	3.00	100.0
25	50	50	15	50	25	25	3.05	99.7
26	50	50	10	50	25			

Iodine sol. = 0.03306 N. Others as in Table III.

Table IV gives the determination of phenol by the same method as used for determining the cresols. The method does not vary from Wilkie's, except that the concentrations of the reagents are so chosen that with continuous shaking for one minute the reaction is complete. This rapid reaction leaves the precipitate a flocculent, white or pinkish mass and does

not obscure the iodine-starch color, requiring thereby no filtering off of the precipitate as in Wilkie's method, which allows ten minutes for the "reaction period" and as a consequence a filtering off of the dark red precipitate is required. In Experiment 26, the 25 minutes' shaking had made the precipitate so dark that the determination could not be made without filtering.

Experiments 19 and 20 show that $N/10$ sodium bicarbonate is not sufficient to complete the reaction in 1 minute. Fifteen minutes are required for its completion under these conditions (Expt. 21). Sodium bicarbonate $N/4$ was used in Expt. 22 and was found to be sufficient with one minute's reaction period. One minute is sufficient time to complete the reaction with $N/2$ bicarbonate and when 25 minutes was allowed for the reaction no further absorption of iodine took place. The precipitate was a lilac-pink. With less phenol and the same amount of iodine (Experiment 26); the precipitate was a dark wine color and obscured the end point in titrating back with thiosulfate for excess iodine. A precipitate appeared in Experiments 19 to 21, but no precipitates formed in Experiments 23 to 26 until the acid was added.

DETERMINATION OF A MIXTURE OF *o*-, *m*- AND *p*-CRESOL

A solution was made up by taking one-third by weight of each of the cresols and diluting until the

TABLE V. DETERMINATION OF MIXTURES OF *o*-, *m*- AND *p*-CRESOLS.

Ex. No.	NaHCO ₃ Cc.	Water Cc.	Cresol mixtures Cc.	Iodine Cc.	Reaction period Min.	2 N acid added Cc.	Thio Cc.	N/10 iodine absorbed Cc.	Calculated iodine absorption Cc.
27	25	75	15	40	1	25	1.5	11.75	11.73
28	25	75	15	40	1	25	1.5	11.75	11.73
29	25	75	14	40	1	25	2.3	10.97	10.95

For solutions, etc., see Table VI.

strength of the solution contained (108.064/60) grams cresols per liter. The results are given in Table V. In the second last column is given the amount of iodine absorbed by the cresols and the last column represents the amount of iodine which should have been absorbed, calculated for the amount of cresols in the solution (reckoning the ortho- and para-cresols as di-iodo-cresols and the meta-cresol as the tri-iodo-cresol). The error in each case is 0.2 per cent and reckoned as an error for any one of the three cresols represents a loss of 0.6 per cent, since they are each present in equal amounts, or if the error be distributed over each of the three ingredients, it is an error in each of 0.2 per cent.

A MIXTURE OF PHENOL, *o*-, *m*- AND *p*-CRESOL

The equation of Ditz to determine the amounts of *m*-cresol in the presence of *o*- or *p*-cresol, and modified later by Siegfried and Zimmermann for determining phenol in the presence of *p*-cresol may be extended to include the determination of phenol, *o*-, *m*- and *p*-cresol in the presence of all four compounds and with these equations, if there be known (1) the weight of the mixture present; (2) the total amount of iodine ab-

sorbed; the following determinations may be made from a single titration.

- (1) The meta-cresol present.
- (2) The phenol present.
- (3) The sum of the *o*- and *p*-cresols present.

If x = weight of (phenol + *m*-cresol).

y = weight of (*o*- and *p*-cresol).

m = Total weight taken of the mixture.

e = effective formula weight of phenol and *m*-cresol.

a = weight of phenol present.

b = amount of *m*-cresol.

n = number of mols of iodine disappearing.

$$\text{Then } x + y = m \quad (1)$$

$$\frac{3x}{e} + \frac{2y}{108.064} = \frac{n}{2} \quad (2)$$

$$a + b = x \quad (3)$$

$$\frac{a}{94.048} + \frac{b}{108.064} = \frac{x}{e} \quad (4)$$

$$\frac{108.064 - e}{e - 94.048} = \frac{108.064 a}{94.048 b} \quad (5)$$

Of the above quantities, n is known and is the amount of iodine disappearing or absorbed:

m is known and is the amount of the mixture of cresols and phenol weighed out into the solution.

x , y , e , a , b are five unknowns, and with the five independent equations given, they may be obtained.

This method is limited since the amount of the mixture m is obtained by weighing, and no impurity can be present without affecting the results. Further, it can be seen from the nature of the equations containing e that small variations in the determination of e affect the value of a and b considerably. However, if the dried precipitate of the iodo compounds were weighed after the titration with the thiosulfate a different value for m would be obtained; m would then represent the weight of the halogenated mixture, not the mixture itself. Equation (1) will become

$$x + y + (127.96) N/2 - (1.008) N/2 = m.$$

The equation is useful for analyzing mixtures containing water and other compounds which do not halogenate and which prevent the weighing of the mixture before precipitation with the iodine. The determination by the iodine and sodium bicarbonate is as accurate as the operator chooses to make it. Using

TABLE VI—DETERMINATION OF MIXTURES OF PHENOL, ORTHO-, META- AND PARA-CRESOL

Ex. No.	NaHCO ₃ Cc.	Water Cc.	Cresol mixture Cc.	Iodine Cc.	Reaction period Min	2 N. acid added Cc.	Thio Cc.	$\frac{e}{a}$ Cc.	Calculated iodine absorption Cc.
30...	25	75	20	60.0	1	25	4.02	15.88	15.99
31...	25	75	20	60.0	1	25	3.83	16.08	15.99
32...	25	75	20	60.0	1	25	3.95	15.96	15.99

Thiosulfate = 0.0982 N. Sulfuric acid = 2 N. Temperature = 23° C.
Iodine = 0.03306 N. Sodium bicarbonate = N.

large volumes of solutions (50 cc.) and allowing at least 8 minutes for the solution to run out of the 50 cc. burettes, very accurate results can be obtained.

Table VI gives the results of three successive titrations of a mixture composed of equal volumes of solutions of phenol, *o*-, *m*- and *p*-cresol having the following strengths:

Phenol = 0.09060 N.

o-Cresol = 0.06800 N.

p-Cresol = 0.06800 N.

m-Cresol = 0.09850 N.

The second last column gives the amount of iodine absorbed by the mixture. The last column gives the amount which should have been absorbed calculated from the amount of materials added to the mixture. The error varies from 2 parts to 5 parts per thousand. If the discrepancy be calculated over the four ingredients the error is 0.2 to 0.5 per cent. If the error be calculated as due to one single substance present the determinations vary by 0.8 to 2.0 per cent, since the substances are present in equal amounts by weight.

DETERMINATION OF THYMOL

The assumption is very general in the literature that time is an important factor in the halogenation of aromatic compounds. This is especially true for the more highly substituted phenolic bodies. Fifteen minutes to one hour is recommended as the time for complete halogenation. The assumption that this rate of reaction is comparatively slow seemed untenable. If complete diffusion be effected by continuous shaking the reaction should be complete in a very short time. To test this, the determination of thymol (3-methyl-6-isopropyl phenol) was undertaken.

The iodine-sodium bicarbonate method was applied to the determination of thymol and the results are given in Table VII. The calculations are made for the thymol strength, assuming that two iodines enter the ring giving di-iodo-thymol.

TABLE VII—DETERMINATION OF THYMOL

Ex. No.	H ₂ O Cc.	NaHCO ₃ Cc.	Thymol Cc.	Iodine Cc.	Reaction period Min.	H ₂ SO ₄ Cc.	20 per cent KI Cc.	Thiosulfate Cc.	Per cent of thymol found
33...	100	25	15	27.4	2	25	..	1.72	100.0
34....	100	25	10	18.0	1	25	..	1.07	100.0
35....	100	25	5	32.25	1	25	..	7.79	122.6
36....	100	25	15	32.0	1	25	..	3.20	100.8
37....	100	25	15	30.0	1	25	5	2.58	100.2

Iodine = 0.03306 N.

Thio = 0.0982 N.

Thymol = 0.0491 N.

Sulfuric acid = 2 N.

Sodium bicarbonate = N.

Temperature = 23° C.

(a) This result was obtained by titrating the blue color, which returned after the first titration. The time allowed for the blue to return was 10 minutes. The blue did not return in one half hour after the second titration.

Experiments 33 and 34 show that the iodination is complete in one minute. Seidel¹ states that one-half hour must be allowed for thymol to be brominated. This is true only in case the diffusion is incomplete. If the free iodine is in excess (300 per cent), as in Experiment 35, the hydroxyl is partly filled with iodine and gives a determination 22 per cent too high, calculated as the di-iodo-thymol. Experiment 36 indicates that the iodine which is absorbed in the hydroxyl will be freed in a few minutes if the precipitate is left in

¹Am. Chem. J., 47, 519 (1912).

contact with the small amount of hydriodic acid, which has been formed in the solution. The reduction can be seen in the rapid return of the blue color. This return of the blue continues only until the iodine in the hydroxyl has been completely liberated. An addition of 5 cc. of 20 per cent KI reduced the di-iodo-thymol bromide in one minute to the di-iodo-thymol and the blue color does not return rapidly (*i. e.*, within one hour).

In working with the cresols and phenol the blue did not return except in the case of the ortho-cresol. The reading was taken after the blue ceased to return (5 to 10 minutes). No KI was added. However, it is advisable to use KI if the experiments show a tendency for the blue color to return within five or ten minutes. The free hydriodic acid produced in the acid solution by this addition reduces¹ the thymol iodide completely, with one minute's shaking. Wilkie states that his determinations were all high (1½ per cent). The explanation lies probably in the fact that the iodine is partly absorbed into the hydroxyl and as the iodo precipitate is filtered off in his method, there is no possibility of its reduction.

DIRECTIONS FOR DETERMINING PHENOLIC COMPOUNDS

First. Solutions required: 0.1 *N* sodium thiosulfate, 24.8 grams per liter; 0.03 *N* iodine solution, 12.7 grams per liter; *N* sodium bicarbonate; 2 *N* sulfuric acid; 0.5 per cent starch solution.

Second. Into a 500 cc. ground stoppered bottle, put 50 cc. water and 50 cc. of approximate *N* sodium bicarbonate, add 15 cc. of the unknown solution of the phenolic compound which has been previously diluted to approximately 0.1 *N*.

Run in the iodine solution until the mixture in the bottle remains a permanent brown iodine color; 20 per cent excess is recommended. Stopper the bottle firmly and shake it well for one minute.

Third. Add carefully, at first, to prevent excessive bubbling, 50 cc. of 2 *N* sulfuric acid. Shake well and titrate the excess iodine with the thiosulfate, using starch as indicator. Occasionally blue color returns rapidly after the end point has been first reached. For such determinations it is best to add 5 cc. of 20 per cent KI to hasten the freeing of the iodine which is held in the hydroxyl. The final end point after the blue ceases to return is the correct reading for the thiosulfate. All the solutions should be at 20°–25° C.

SUMMARY

I. Rapid and accurate determinations of *o*-, *m*-, and *p*-cresol, phenol and thymol have been effected by the use of iodine solutions in the presence of sodium bicarbonate.

II. The method is equally rapid and accurate for all five compounds, the error for each compound being within 0.2 per cent.

III. The "reaction period" for these determinations is one minute, when the shaking is continuous.

IV. The sum of the cresols present in a mixture may be determined within a total error of 0.2 per cent;

the *m*-cresol may be determined in the presence of *o*- and *p*-cresol by this method.

V. A series of simple equations are given which will permit the determination of phenol, meta-cresol and the sum of the ortho- and para-cresols in the presence of each other in any combination or proportion if two quantities be known.

(a) The weight of the mixtures taken.

(b) The amount of iodine absorbed.

VI. Results of experiments are given which show that these four compounds can be determined in the presence of each other by this method within an error of 0.2 to 0.6 per cent, calculated on the sum of the materials present.

DEPARTMENT OF INDUSTRIAL RESEARCH
UNIVERSITY OF KANSAS
LAWRENCE

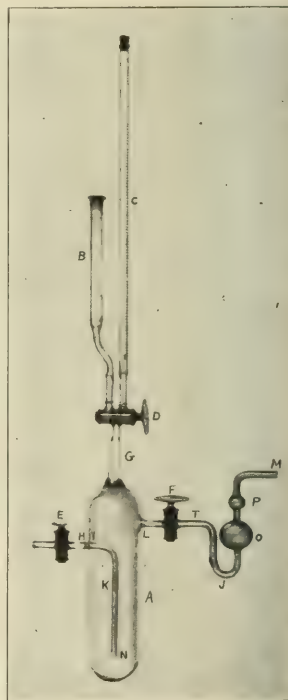
AN APPARATUS AND METHOD FOR DETERMINING HYDROGEN SULFIDE IN ILLUMINATING GAS¹

By E. P. HARDING AND EINER JOHNSON

Received July 28, 1913

The apparatus herein described was designed as a means of testing the efficiency of a set of gas purifiers such as are used in the manufacture of coal gas or carburetted water gas for illuminating purposes. It combines the accuracy of the gravimetric cadmium chloride method and the rapidity of the Tutwiler method.²

The apparatus consists of a bulb, A, of 300 cc. capacity about 18 cm. long and 5 cm. in diameter, sealed at the lower end and contracted at the top to 13 mm. To the contracted end is fused the tube G, terminating in a Greiner and Friedrichs stopcock, D, to which is fused burettes B and C, each having a capacity of 10 cc. Burette B is 20 cm. long and 13 mm. in diameter calibrated in the middle portion. C is 34 cm. long and 10 mm. in diameter graduated into 10 cc. and reading to tenths of one cc. Both B and C are fitted with stoppers. To one side of bulb A at L, 14 cm. from the base of A, is attached tube T 7 mm.



¹ Published in abstract in Proceedings of the 8th International Congress.

² *J. Am. Chem. Soc.*, **23**, 173

¹ *Werner Jahresber.*, 633 (1886) Lloyd, *J. Am. Chem. Soc.*, **27**, 16 (1905).

in diameter and terminating at M bearing a stopcock, F, 25 mm. from L, a U tube, J, a bulb, O, of 10 cc. capacity and a bulb, P, 2 cc. in capacity. To the opposite side of bulb A at H, 12 cm. from the base of A, is fused tube K 7 mm. in diameter beginning at I and extending into the bulb and terminating at N, 20 mm. from its base. K bears the stopcock E, 30 mm. from H. S is a clamp which supports the apparatus. When passing gas through the apparatus it is supported by placing it in a hole in a block of wood.

In making a determination, from 100 to 150 cc. of a strong solution of cadmium chloride are run into bulb A, stopcock F being open and E closed. The apparatus is then tilted in such a position that 5 or 6 cc. of the solution pass into bulb O which acts as a seal and indicator preventing traces of hydrogen sulfide from escaping unabsorbed and indicating when the cadmium chloride solution in A is nearly spent. Bulb P prevents traces of solution in O from being carried from the apparatus.

Burette C is filled with a standard solution of iodine, two solutions of different iodine strengths being used, one containing 4.828 grams of iodine per liter and another one-tenth as strong. The strong solution is of such a strength that 1 cc. is equivalent to 10 grains of hydrogen sulfide per 100 cubic feet when one-tenth of a cubic foot of gas is used in the determination and is used in testing the crude gas while the weaker solution is used in testing partially purified gas. Stopcock D is closed and A is connected at M with the meter and at I with the gas supply cock by means of rubber tubing. The meter is read, E is opened and the flow of gas so regulated that from 1 to 1.5 cubic feet pass through the apparatus per hour. When a color appears in bulb O, the gas is shut off by closing stopcock E and the meter reading taken. In testing partially purified gas when no color has appeared in O after one-tenth cubic foot of gas has passed but when a perceptible precipitate has formed in A, the gas supply is cut off. If a perceptible precipitate has not appeared in A after one-tenth cubic foot has passed, the flow is continued until one does appear.

The apparatus is disconnected from the meter and gas supply, removed from its support, D opened and then so tilted that the solution in O runs back into A. Wash water is drawn in through M by applying suction at top of B and through K by opening E, closing F and applying suction at top of B. The gas above the solution in A is removed by opening F and applying suction at top of B. D is closed and fresh starch solution run into B, then D is opened and the starch solution run into A. E and F are closed and the air in A placed under diminished pressure by applying suction at top of B. D is then closed and B is filled with concentrated hydrochloric acid which is allowed to pass slowly into A until the precipitate of cadmium sulfide is completely dissolved. A little excess of hydrochloric acid is then run in and D closed. The hydrogen sulfide thus liberated in A under diminished pressure and out of contact with air is titrated with the iodine solution. Burette C is read and the iodine

solution introduced intermittently by carefully opening D, the apparatus being shaken after each addition. When the starch-iodo blue color persists for one-half minute, the end point in the titration has been reached. (The pink or violet color which first appears in the solution must be distinguished from the starch-iodo blue which is the correct end point.) C is then read. The apparatus is then emptied, rinsed with water and a blank test run to determine the amount of iodine solution necessary to produce the permanent starch-iodo blue color. In making this test the same amount of starch solution and the same volume of water as is used in the determination is used and the whole acidified with hydrochloric acid. From the amount of gas and the volume of iodine solution used in the determination and in the blank, the number of grains of hydrogen sulfide per 100 cubic feet of gas is calculated. For control work the volume of gas used need not be reduced to its corresponding volume at standard conditions of temperature and pressure.

Comparative determinations of hydrogen sulfide were made by the gravimetric cadmium chloride, the Tutwiler and the volumetric cadmium chloride methods. In these determinations the meters used were dry meters checked against each other, the samples were taken simultaneously and the volume of gas used reduced to corresponding volume at standard conditions of temperature and pressure by means of the following formulae:

$$V = v \cdot \frac{17.64 (h - a)}{460 + t} \cdot n = \frac{17.64 (h - a)}{460 + t}$$

$V = vn$ where

V = volume of gas at 60° F. and 30" pressure.

v = observed volume.

t = observed temperature in Fahrenheit degrees.

h = observed barometric pressure.

a = tension of aqueous vapor at t .

n = correction factor for t and h .

The following results in grains, cadmium chloride, CdCl_2 , per 100 cubic feet were obtained:

Grav.	Vol.	Tutwiler	Grav.	Vol.	Tutwiler	Grav.	Vol.	Tutwiler
Coal gas								
2.72	2.93	31	1.81	1.72	27	0.59	0.55	16
0.53	0.46	22	0.88	0.84	18	0.26	0.23	8
0.89	0.79	27	4.86	4.76	110	0.40	0.36	11
1.58	1.54	38	2.73	2.69	65	0.15	0.13	5
1.00	0.92	24	1.22	1.18	28	0.34	0.31	12
2.68	2.65	30	2.72	2.61	28	Crude coal gas		
1.31	1.25	23	1.65	1.59	30	225.0	220.0	360.0
2.35	2.26	29	1.30	1.26	26	190.0	188.0	310
			1.09	1.04	24			

The uniformly higher results obtained by the gravimetric method may be due to the absorption of other sulfur compounds than hydrogen sulfide, a much larger volume of gas and cadmium chloride solution being used in the gravimetric method than in the volumetric method.

The principal advantage of Tutwiler's method is its rapidity. A test can be made in about three minutes. Its chief disadvantage is its inaccuracy. The results obtained are only approximate especially

on the partially purified gas, the error varying from 1000 to 4000 per cent as shown by the comparative tests above. This error is due to the titration of the gas with the iodine solution, the unsaturated hydrocarbons, cyclopentadiene¹ and probably sulfur compounds other than hydrogen sulfide reacting with the iodine. Results on the crude gas are less inaccurate, the error amounting to about 15 per cent. This is of course due to the much greater ratio between the amount of hydrogen sulfide present and the other compounds with which the iodine reacts. McMillar states in the original publication of Tutwiler's method that 15 grains of hydrogen sulfide per 100 cubic feet of gas could escape detection. In the writers' experiments, in no case did the Tutwiler show less than 10 grains per 100 cubic feet on clean coal gas nor less than 4 grains per 100 cubic feet on clean water gas.

The gravimetric cadmium chloride method is the most accurate in use at the present time. The great objection to this method, however, in control work is the length of time required to make a determination. The purifying boxes foul quite rapidly and in determining their efficiency tests should be made rapidly and as nearly simultaneously at inlet and outlet of purifier as possible. A method which requires hours for a test becomes impracticable. The large bulk of cadmium chloride solution used allows absorption of other sulfur compounds than hydrogen sulfide, which when oxidized with the bromine give too high results. Another objection is the large amount of cadmium sulfide precipitate required to produce an amount of barium sulfate which can be readily and accurately weighed. When a sample of 0.1 cubic foot of gas is taken, each milligram of BaSO₄ is equivalent to 2.252 grains of sulfur per 100 cubic feet. Thus for partially purified gas containing but a fraction of one grain of hydrogen sulfide per 100 cubic feet, a number of cubic feet of gas must be used in order to obtain a weighable precipitate.

The volumetric cadmium chloride method has several advantages over the gravimetric method. Accurate results are obtained on a much smaller volume of gas; a smaller volume of cadmium chloride solution causes less absorption of sulfur compounds other than hydrogen sulfide; the method is much more rapid, requiring for a determination instead of hours, from seven to ten minutes, depending upon the purity of the gas.

The advantages of the volumetric cadmium chloride method over the Tutwiler are several. Twenty-eight times as much gas is used in the average determination as is used in the Tutwiler; the burette readings are one-tenth those of the Tutwiler and much more accurate results on gas of low hydrogen sulfide content are obtained. A test can be made in from seven to ten minutes.

Instead of a meter, a graduated cubic foot bottle may be employed for measuring the volume of gas used.

UNIVERSITY OF MINNESOTA
MINNEAPOLIS

A METHOD FOR THE DETERMINATION OF PHOSPHORUS IN VANADIUM STEEL AND FERRO-VANADIUM

By C. F. SIDENER AND P. M. SKARTVEDT

Received July 21, 1913

This paper embodies the adaptation of some well-known reactions to the determination of phosphorus in vanadium steel and ferro-vanadium, together with results obtained by the method, which is as follows: The sample is dissolved in dilute nitric acid. If an insoluble metallic residue remains, a little hydrochloric acid is also added. The solution thus obtained is evaporated to dryness and baked until the nitrate of iron is decomposed. The residue is dissolved in concentrated hydrochloric acid and about 0.02 gram of aluminium in the form of aluminium chloride is added. The solution is nearly neutralized with ammonia, heated almost to boiling, and the iron reduced by the gradual addition of a concentrated ammonium bisulfite solution with stirring. The reduction is best accomplished by keeping the solution slightly acid until nearly reduced, and then adding ammonia until a slight permanent precipitate of iron hydroxide remains after vigorous stirring, finally dissolving the precipitate with a few drops of ammonium bisulfite. To the solution, now smelling quite strongly of sulfur dioxide, one or two cc. of phenylhydrazine¹ are added drop by drop with stirring. If no precipitate appears, a few drops of ammonia are added until a slight permanent precipitate is formed. Then a few drops more of phenylhydrazine are added to complete the precipitation. The solution is boiled about two minutes, allowed to settle and filtered.

This precipitate consists of aluminium phosphate, aluminium hydroxide and more or less of the vanadium. After washing with hot water until the washings show no cloudiness when tested with mercuric chloride, the precipitate is dissolved off the filter into the original beaker with dilute nitric acid.

In the nitric acid solution containing the phosphorus and vanadium, the latter is oxidized by the addition of a little hydrogen peroxide, and then a slight excess of sodium carbonate is added. The solution is boiled for about five minutes and the phosphorus precipitated as aluminium phosphate by gradually adding dilute nitric acid until the solution no longer gives an immediate brown tinge to turmeric paper.² It is important that this point be very carefully noted. The precipitate is filtered off and washed with a 1 per cent solution of ammonium nitrate. It is then dissolved off the filter into an Erlenmeyer flask with dilute nitric acid and a little hydrogen peroxide added, which will produce a deep red color if much vanadium is present and a pinkish yellow if but a trace is present. If this test shows the presence of even a trace of vanadium, another precipitation with sodium carbonate and nitric acid is necessary. The number of precipitations required to separate the phosphorus from the vanadium depends upon the amount of vanadium in the sample. For those containing up to 1 per cent, a single precipitation is sufficient; 1 to 5 per cent, two precipita-

¹ Hess and Campbell, *J. Am. Chem. Soc.*, **21**, 770.

² C. M. Johnson, "Chemical Analysis of Special Steels," p. 26.

tions; and from 5 to 30 per cent, two and often three.

To the nitric acid solution is now added ammonium molybdate to precipitate the phosphorus which is determined by the permanganate oxidation method in the usual manner. If the vanadium has not been completely separated from the phosphorus it will be indicated by the orange color of the ammonium phosphomolybdate precipitate which is quite characteristic; also by the tendency of the precipitate to form quickly and adhere to the glass.

Results obtained by this method are given in the following tables: Table I shows the results obtained from a mixture of standard solutions containing iron, phosphorus and vanadium in proportions approximately those found in vanadium steels.

TABLE I

Iron taken, 1 gram; vanadium, 6.75 mg. in first 11 and 27 mg. in last four experiments; phosphorus, 2 mg. The actual weight of phosphorus varied from 1.38 mg to 2.40 mg., but for convenience of comparison all were calculated to a 2 mg. basis.

Milligrams of phosphorus found

2.01	1.98	2.01	2.07	1.97
2.03	2.13	2.00	2.01	1.99
2.03	1.95	1.97	2.08	1.98

TABLE II—RESULTS ON A BUREAU OF STANDARDS VANADIUM STEEL CONTAINING 0.15 PER CENT VANADIUM AND 0.035 PER CENT PHOSPHORUS

No	Grams steel taken	Percentage phosphorus found
1.....	1.2377	0.0353
2.....	0.8329	0.0352
3.....	2.9114	0.0340
4.....	2.5538	0.0350
5.....	3.5430	0.0347
6.....	3.9635	0.0356

TABLE III—RESULTS ON TWO BUREAU OF STANDARD STEELS TO WHICH WAS ADDED VANADIUM IN VARIOUS AMOUNTS FROM 0.5 PER CENT UP TO 30 PER CENT OF THE WHOLE WEIGHT TAKEN

	Steel taken Grams	Percentage vanadium added	Percentage phosphorus in the steel	Percentage phosphorus found
1.....	1.4102	0.5	0.093	0.096
2.....	1.5759	0.5	0.093	0.092
3.....	1.4749	0.5	0.093	0.0917
4.....	1.5297	0.5	0.093	0.094
5.....	1.5090	0.5	0.093	0.101
6.....	1.5015	0.5	0.093	0.108
7.....	1.5022	0.5	0.093	0.097
8.....	1.5019	0.5	0.093	0.089
9.....	1.0462	1	0.112	0.110
10.....	1.0088	1	0.112	0.113
11.....	1.2064	1	0.112	0.111
12.....	1.1623	1	0.112	0.109
13.....	1.0244	5	0.112	0.107
14.....	1.0469	5	0.112	0.119
15.....	0.9995	5	0.112	0.113
16.....	1.0092	20	0.112	0.116
17.....	1.0055	20	0.112	0.111
18.....	1.0040	20	0.112	0.111
19.....	1.0077	30	0.112	0.102
20.....	1.0095	30	0.112	0.103
21.....	1.0107	30	0.112	0.106
22.....	1.0092	30	0.112	0.114

Although some of the results in the above tables are not as concordant as might be desired, yet it is believed that they may be taken as satisfactory for so troublesome a determination.

A FUSION METHOD FOR THE DETERMINATION OF SULFUR IN IRON AND STEEL

BY FREDERICK H. FRANKLIN¹

Received June 6, 1913

The accurate determination of sulfur in iron and steel presents many difficulties, owing to the extremely variable and complex nature of the iron-carbon alloys. It has been shown that sulfur combines with manganese in preference to iron.² Therefore, in most commercial iron and steel alloys we have to deal with the former sulfide. It has been found that the insoluble residue left on dissolving iron for the sulfur determination usually contains some sulfur and this must be determined in accurate work. It is also well known that when much cementite is present volatile compounds of sulfur and carbon are formed which are difficult to oxidize and so escape estimation. It may readily be seen therefore that the method employed should be capable of giving a correct measure of the total sulfur no matter whether it exists in one or all of the above combinations.

For the purposes of this paper it will be sufficient to describe briefly one representative from each of the two principal classes into which the sulfur methods may be divided.

The volumetric or evolution method is in very general use and is usually modified by its advocates to meet the existing conditions. The gravimetric or oxidation method possesses some advantages over the former and is believed to be the most accurate method now in use. Both of these methods have a multitude of modifications and the mere statement that sulfur was determined by the volumetric or by the gravimetric method is no proof that the figures reported are the most accurate obtainable by the class chosen.

The Volumetric or Evolution Method.—In its simplest form this method consists of dissolving the metal in 1.1 sp. gr. hydrochloric acid and passing the evolved gases through an ammoniacal solution of cadmium chloride. The mixture of cadmium sulfide and dilute ammonia is acidified with hydrochloric acid and titrated with a solution of iodine that has been standardized either against sodium thiosulfate or iron of known sulfur content. The chief advantages of this method lie in its rapidity and the index of the amount of sulfur afforded by the precipitated sulfide. For most irons and steels this method when properly carried out gives results that agree fairly well with those obtained by the gravimetric method.

To overcome the shortcomings of the method some authors propose annealing the drillings which by changing cementite, martensite, etc., into pearlite, prevents loss of sulfur as volatile compounds. It is also claimed by other writers that by passing the evolved gases through a red hot tube, the carbon-sulfur compounds are broken down to hydrogen sulfide.

A German Commission,³ appointed by the Verein Deutscher Eisenhüttenleute to investigate the de-

¹ Cf. Saunders and Franklin, Official chemists for the New England Drymen's Association.

² Carnot and Goutal, *Compt. rend.*, 1897, 125; J. C. S., 1897, 72.

³ Schwefelbestimmung in Eisen u. Stahl. *Stahl u. Eisen*, 28. Jahr. Nr. 8

termination of sulfur in iron and steel, considered the use of hydrochloric acid of 1.10 sp. gr. absolutely necessary and that when used, the passage of the evolved gases through a red hot tube can be dispensed with.

T. Gifford Elliot,¹ in the *Journal of the Iron and Steel Institute*, combines the annealing and strong hydrochloric acid modifications and when titrating runs in an excess of standard iodine solution and titrates back with sodium thiosulfate.

The Gravimetric or Oxidation Method. This is usually executed by dissolving the iron or steel in strong nitric acid. The solution is evaporated to dryness, baked, redissolved in strong hydrochloric acid, diluted, filtered and the sulfur precipitated as barium sulfate. This method is also modified at several stages,² the most important of which are solution in nitric acid and removal of excess acid before precipitation of barium sulfate.

Potassium bromide and chlorate are used by Noyes to prevent loss of sulfur during solution and the same author separates the iron by ammonia before precipitating the barium sulfate. In nearly all methods, however, the barium sulfate is formed in the presence of a large amount of ferric chloride and no attention is paid to the iron retained by the barium sulfate.

That the oxidation method has many failings is indicated by the numerous attempts to overcome them by modifications. This is one of the principal reasons that led to the development of the new method which is called the Fusion Method and is the result of a search for a method capable of giving accurate results with any kind of iron. It was desired that solution of the iron be effected without the use of acids and that the sulfur be precipitated as barium sulfate without the presence of iron salts.

Having observed that the carbonaceous residue obtained by the solution of iron in copper-potassium chloride solution contained sulfur, an experiment was carried out to learn how much of the total sulfur it contained.

A few grams of cupola iron (pig iron remelted in the cupola) were dissolved in a solution of copper-potassium chloride and filtered through asbestos. The carbonaceous residue was mixed with sodium carbonate, sodium peroxide and a little sugar, then ignited by a hot wire. The aqueous solution of the fusion was acidified with hydrochloric acid heated to boiling and the sulfur precipitated by barium chloride. The results were surprising, giving a greater percentage of sulfur than was obtained by the volumetric method.

A large number of experiments were carried out and all results agreed closely with the gravimetric figures. A search through the literature on sulfur was made and the nearest approach to this method was found in an article by C. Meineke in *Zeitschrift für angewandte Chemie*.³ The author dissolves the iron by boiling with a solution of copper-ammonium chloride,

acidified with hydrochloric acid, and then after filtering off the insoluble, dissolves it in an oxidizing acid and, after evaporating to dehydrate silica, filters and precipitates sulfur as barium sulfate.

THE FUSION METHOD

This method is given with considerable detail, not because this is necessary for accurate results but because of a desire to assist those who are not familiar with the technique of the operations involved.

The sample should be prepared with care and should be moderately fine; drillings made slowly with a rather dull drill are best.

SOLUTIONS, ETC., REQUIRED FOR THE FUSION METHOD

Copper Potassium Barium Chloride Solution. Dissolve 600 grams of copper-potassium chloride in warm water, add 30 cc. of hydrochloric acid, 30 cc. of barium chloride solution, and dilute to 1600 cc. After standing 24 hours, filter through asbestos.

Sodium Peroxide is practically free from sulfur.

Anhydrous Sodium Carbonate is free from sulfur.

Barium Chloride Solution of 20 per cent strength.

Hydrochloric Acid, C. P., has a density of about 1.19.

Dilute Hydrochloric Acid.—Add 100 cc. of hydrochloric acid to 900 cc. of distilled water.

Asbestos Suspension.—The acid-washed fiber is ignited and again washed with dilute hydrochloric acid and kept suspended in water.

Dissolve 3 grams of sample in about 120 cc. of copper-potassium chloride solution containing barium chloride, by means of a suitable stirring device. A Juno motor in series with an incandescent lamp gave excellent service. Allow the solution to stand about thirty minutes, then decant upon an asbestos pad formed in a porcelain Gooch crucible, using suction to hasten filtration. Wash the residue into the crucible by means of a fine stream of dilute hydrochloric acid, using as little as possible. After acid has run through, add just enough fine asbestos suspension to cover the carbonaceous residue. Finish washing with 15 to 20 cc. of warm water.

After all has passed through, wash down the sides of the crucible with a few drops of alcohol. Remove the pad and residue with tweezers, an operation easily accomplished if the crucible has a removable bottom. Separate the asbestos as completely as possible and dry the black residue at a temperature slightly under 100° C. for about 15 minutes.

Weigh 3 grams of anhydrous sodium carbonate and mix with it the dried residue by means of a small glass mortar and pestle.

Transfer to a nickel crucible of 20 cc. capacity and incorporate 3 grams of sodium peroxide. Place the covered crucible over a small flame and heat till the gentle oxidation is completed and the melt is quiet and homogeneous. This operation requires only about 2 or 3 minutes and should not be continued longer or much nickel will be dissolved.

While the melt is solidifying, cause it to cover the sides of the crucible. Rinse off the outside of the crucible and place in a small beaker containing 50 cc. of hot water and warm until the fused mass is de-

¹ "The Volumetric Estimation of Sulfur in Iron and Steel," *J. I. S. I.*, 1911, No. 1.

² Bamber, *J. I. S. I.*, 1, 319 (1894).

³ Abstract in *Chem. News*, March 1, 1889.

tached. After removing and rinsing the crucible, add 15 cc. of hydrochloric acid, using precautions to prevent loss.

After boiling this solution until clear, evaporate to dryness in platinum and heat in oven at 130°–135° C. to dehydrate silicic acid. Dissolve the residue in 50 cc. of distilled water containing 1 cc. of hydrochloric acid, filter and wash until a filtrate of about 90 cc. is obtained. Heat to near the boiling point and add 7 cc. of hot 20 per cent barium chloride solution, drop by drop, keeping the temperature near the boiling point. A Schuster dropping flask (shaped like a tiny retort) is convenient for this purpose. Keep the beaker with the precipitate warm for some time and allow to stand over night or about 15 hours. Collect the barium sulfate on an asbestos pad in a platinum Gooch crucible, wash, ignite and weigh.

With steels and low silicon irons the method may be shortened by omitting the evaporation to remove silica, if the amount of asbestos fused with the residue is not large. Should a slight precipitate of manganese dioxide appear it may be dissolved by the addition of a minute crystal of tartaric acid, which usually produces a sparkling light green solution.

In the following table of results, those obtained by the volumetric method are marked *v*, and those by the gravimetric, *g*:

TABLE OF RESULTS

Sample	Percentage Sulfur	Percentages sulfur	
		Fusion method	Other methods
Bureau of Standards			
C renewal.....	0.035	0.039	0.032 g
B.....	0.039	0.038	0.042 g
B.....	0.039	0.044	0.036 v
B.....	0.039	0.041	
C 2nd.....	0.034	0.032	
C 2nd.....	0.034	0.036	
C 2nd.....	0.034	0.043	
D 3rd.....	0.035	0.036	0.041 g
D 3rd.....	0.035	0.041	0.036 v
0.4 Bes steel	0.118	0.124	0.115 g
Amer. Fdy. Assn., A	0.056	0.057	
	Number		
Cupola iron	38676	0.177	0.155 v
	21678	0.123	0.113 v
	37485	0.108	0.105 v
	39991	0.102	0.097 v
	39345	0.160	0.130 v
	34345	0.116	0.101 v
	40103	0.165	0.147 v
	16519	0.128	0.105 v
	16450	0.124	0.107 v
	16419	0.126	0.119 v
	30253	0.098	0.092 v
	16519	0.128	0.116 g
	41173	0.131	0.096 v
	39345	0.170	0.130 v
Pig irons	(C = 0.76%)	0.054	0.054 v
	30402	0.053	0.040 v
	29765	0.078	0.074 v
	29949	0.047	0.047 v
	29949	0.051	
	2789	0.095	0.084 g
	18169	0.049	0.044 g
White irons			
Chilled roll ..		0.170	0.160 v
Malleable, as cast	41652	0.148	0.095 v
Malleable, as cast	41780	0.168	0.128 v
Low sulfur steel.....	...	0.014	0.010 g

Numerous blank tests were run, using regular amounts of reagents under the same conditions as the analyses themselves and the average amount of sulfur found was 0.0013 per cent.

EXPERIMENTAL

It was thought at first that all the sulfur would not be obtained in the carbonaceous residue but my earliest experiments always gave results that agreed well with the analyses of the Bureau of Standard samples. Carnot and Goutal¹ have shown that "When iron or steel is heated with dilute acids, almost all the sulfur is converted into hydrogen sulfide but when the solvent is a neutral or faintly acid solution of copper-potassium chloride all of the sulfur remains in the residue, partly as ferrous sulfide, but often mainly as cupric sulfide. Direct examination shows that the copper solution has no effect on ferrous sulfide and it follows that the sulfur is partly present in the metal as some other sulfide. Direct examination also shows that the sulfur in combination with copper in the residue is equivalent to the manganese in the iron or steel. Hence part of the sulfur is in combination with manganese as manganous sulfide."

Should any sulfur pass into solution it will immediately form barium sulfate with the excess of barium chloride present in the solvent. Moreover, the solvent is saturated with barium sulfate so that precipitation is immediate.

A few experiments in support of these views and some others which show the effect of free hydrochloric acid on the solubility of barium sulfate are given below:

Barium Sulfate is Carried Down by Carbon

I—4 cc. of BaCl₂ solution were added to a 1 gram sample of shot iron while dissolving in copper-potassium chloride solution. After filtering as usual, 2 grams of granular zinc were added and the solution rotated rapidly till clear. No precipitate was found in hours.

II—Sample treated as in preceding experiment but 2 cc. of N/20 H₂SO₄ were added before filtering. Copper was removed by granular zinc but no precipitate found.

III—To the last test (II), 2 cc. N/20 H₂SO₄ were added and a precipitate formed immediately.

Barium Sulfate is Insoluble in the Ferrous-Cuprous Solution

IV—2 grams of pig iron dissolved in CuKBaCl solution gave 0.096 per cent S or 0.0140 gram BaSO₄.

V—2 grams of pig iron dissolved as before and 2 cc. of N/20 H₂SO₄ added, stirred 5 minutes longer and allowed to settle forty-five minutes on oven. BaSO₄ precipitate could be distinctly seen. The iron contained the equivalent of 0.0140 gram of BaSO₄ and 0.0116 gram was added giving a total of 0.0256 gram and 0.0245 gram was found. Results but 0.001 gram low, showing practically no loss of BaSO₄.

Barium Sulfate is Precipitated Immediately and Completely

VI—2 grams of high sulfur iron (S = 0.27 per cent) were dissolved in CuKBaCl solution. Remained on oven one hour and filtered. The filtrate divided into two portions.

A Placed in long Nessler tube and kept on oven 24 hours. No precipitate visible. After filtering through Gooch, no gain in weight. Absence of BaSO₄.

B Placed in long Nessler tube and 1 cc. of H₂SO₄ (= 0.006 gram of BaSO₄) added. After standing on oven 2 hours, precipitate of BaSO₄ was distinctly visible. After 24 hours, filtered on Gooch and weighed 0.007 gram. The residue was tinged with iron oxide.

To Learn if BaSO₄ Separates from High Sulfur Samples on Long Standing

VII—3 samples of cast iron, 47006–47007–47008, were carried

¹ Loc. cit.

through for sulfur, using CuKBaCl solution and gave

Percentages sulfur

No	Fusion method	Vol. method
47006	0.146	0.144
47007	0.121	0.109
47008	lost	0.106

The filtrates from above stood on the oven for 4 days, then were filtered through paper and carefully washed with dilute HCl and water.

They weighed as follows:

47006	0.0014 gram
47007	0.0050 gram
47008	0.0025 gram

These tests deposited basic salts while standing on oven, to dissolve which they were treated twice with 2 cc. of HCl , but this did not prevent appearance of basic salts. On filtering no indication of BaSO_4 was noted and only an iron stain remained on paper. The 3 filter papers were ignited and weighed separately, then combined and fused with Na_2CO_3 , the solution made faintly acid with HCl and evaporated to crystals. The residue was dissolved in 10 cc. of water and only a slight flocculent precipitate was visible (SiO_2 ?).

Effect of Hydrochloric Acid on the Solubility of Barium Sulfate

VIII—Four solutions were prepared, each containing 3 grams of sodium carbonate and sodium peroxide, made just acid to methyl orange with HCl . 5 cc. $N/20$ H_2SO_4 were added to each (=0.0294 gram BaSO_4).

HCl was added in increasing amounts to each test as follows:

	1	2	3	4
HCl	0.25 cc.	0.50 cc.	1.00 cc.	2.00 cc.

Tests were heated to boiling and slowly precipitated with 7 cc. hot BaCl_2 solution, using a Schuster bottle. Volume = 100 cc. All precipitates were granular and settled rapidly. All precipitates were collected on a carefully prepared asbestos pad and the following results were obtained:

	1	2	3	4
Gram BaSO_4	0.0303	0.0304	0.0290	0.0312
184 WHITTIER AVE PROVIDENCE, R. I.				

THE ANALYSIS OF ALLOYS OF LEAD, TIN, ANTIMONY AND COPPER

By D. J. DEMOREST

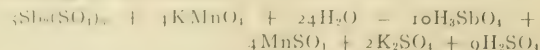
Received June 2, 1913

The following method of analysis has been devised after making hundreds of determinations on alloys and mixtures of metals. The earlier results were inaccurate but they showed the sources of error and ways for improvement in the manipulation until the method as here presented is, in the writer's opinion, the best method for obtaining quick and fairly accurate results in the analysis of the alloys of the above named metals.

The results obtained are reliable to within 0.2 per cent for lead, tin and antimony and 0.1 per cent for copper.

When fine shavings of an alloy containing any or all of the metals lead, tin, antimony, and copper are digested at a boiling heat with concentrated sulfuric acid, the lead is left insoluble as PbSO_4 while the tin goes into solution as $\text{Sn}(\text{SO}_4)_2$, copper as CuSO_4 , and antimony as $\text{Sb}_2(\text{SO}_4)_3$. The lead sulfate is filtered off and weighed and the antimony in the filtrate is

titrated with standard permanganate solution according to the reaction:



After the antimony is titrated, the tin is reduced with iron in the presence of precipitated antimony and the stannous iron is titrated by standard iodine solution.

In another sample the lead is separated as above, and from the filtrate from the lead sulfate the copper is precipitated as CuCNS either with or without a previous titration of the antimony as the chemist may prefer. The CuCNS is then titrated with KMnO_4 or the copper is determined by the very accurate iodide method.

The new things about this method are: *First*, the titration of the antimony by permanganate in a sulfuric acid solution free from HCl ; *second*, the combination of these four methods for lead, antimony, tin, and copper; and *third*, the manipulation necessary for the combination. A great many determinations were made before the manipulation necessary to obtain accurate results was worked out. It is necessary that the details as here given be strictly adhered to, but this is easily done.

Procedure.—Place 1 gram of fine shavings or drillings in a Kjeldahl flask with a short neck, and add 20 cc. of concentrated sulfuric acid. Heat nearly to boiling and continue the heating until the sample is nearly decomposed and the lead sulfate is white. This may take one-half hour. Finally boil for several minutes. Cool the solution and then add 50 cc. of water while the solution in the flask is kept agitated. Heat the liquid to boiling and keep boiling for several minutes. This is necessary to get the antimony sulfate completely into solution, as it crystallizes out from a cold concentrated sulfuric acid solution. Allow the lead sulfate to settle out for about five minutes or until the solution is clear, but do not allow the temperature of the liquid to fall below about 60°C . The liquid above the PbSO_4 should become clear quickly. If it does not, it should be heated longer. After the liquid has become clear, pour it through a weighed Gooch crucible with an asbestos mat. Pour the solution off as completely as possible without allowing more than a very small amount of the PbSO_4 to go over into the crucible.

Now introduce 10 cc. more of concentrated sulfuric acid into the Kjeldahl and heat to boiling and keep boiling several minutes, cool, add 30 cc. of water, heat to boiling for a few minutes, allow the solution to cool to about 50°C . and pour it and the precipitate of lead sulfate into the Gooch crucible. Wash the crucible and precipitate six or eight times with distilled water, taking care to keep the volume of the filtrate down to 125–150 cc. Ignite the PbSO_4 at a dull red heat, preferably in a muffle furnace, for fifteen minutes or more, cool and weigh. It contains 68.3 per cent lead.

Pour the filtrate from the PbSO_4 into a 450 cc. Erlenmeyer flask, heat to 60° – 80°C . and titrate the antimony with standard permanganate of about

N/10 strength. After some permanganate has been run in, the solution takes on a pink tinge but the addition of the permanganate is continued until the color becomes a deep permanganate; then two or three cc. more of permanganate are added. Stir the solution for a minute then titrate the excess permanganate with a standard ferrous sulfate solution until the pink just disappears. This is the end point and it is quite sharp.

The permanganate should be standardized by dissolving 0.2 gram of pure antimony in 30 cc. of boiling concentrated sulfuric acid and, after diluting to 150 cc., titrating with permanganate at 70° C. Fairly close results may be obtained by calculating the antimony strength of permanganate from its iron value by multiplying the iron value by 1.076, but it is much better to standardize against pure antimony.

After the antimony is titrated, the tin is determined according to the method of Low improved by Patrick and Wilsnack.¹ Add to the solution 50 cc. of hydrochloric acid and about 0.15 gram of antimony dissolved in 5 cc. of concentrated sulfuric acid unless there is already that amount of antimony present, in which case no antimony need be added. Insert into the neck of the flask a three-hole rubber stopper. Through one hole pass a glass tube which reaches to the bottom of the flask. Between the stopper and the flask and opposite the other holes, pass a platinum wire on the end of which is a sheet of pure iron (such as ingot iron) about two inches long and one-half inch wide, which rests on the bottom of the flask. Pass CO₂ or hydrogen or natural gas (which has bubbled through NaOH solution to remove H₂S) through the glass tube, and heat the solution to slow boiling; continue the boiling and the stream of gas for thirty minutes after the solution has become colorless. The antimony precipitates out and with the iron reduces the tin to the divalent condition. Cool the solution while a rapid stream of the gas is kept passing through the flask to keep out air. When cold add through a funnel in one of the holes in the stopper 100 cc. of cold, recently boiled, distilled water containing several cc. of starch solution. Pull the iron sheet up out of the solution by means of the platinum wire. Remove the funnel and while a slow current of gas is passing, insert the tip of a burette through one of the holes and titrate the tin with a *N*/10 iodine solution until a blue color is obtained. The end point is very sharp but will fade after several minutes. The results are quite accurate.

At the same time that the above sample is being analyzed, another sample should be similarly treated up to or through the antimony titration, if the chemist desires duplicate results on the lead and antimony. To the sulfuric acid solution add three grams of tartaric acid, next ammonia until the solution is slightly alkaline, and then two cc. of sulfuric acid; heat nearly to boiling. Add two grams of sodium sulfite and when it is all dissolved add a gram of KCNS dissolved in 10 cc. of water. Shake the flask well and allow the CuCNS to settle for fifteen minutes while the solution

is kept hot. Filter through an asbestos mat, wash well with water, and determine the copper in the precipitate by either the sulfocyanate-permanganate method or by the iodide method after igniting the precipitate and dissolving the copper oxide in nitric acid.

NOTES ON THE PROCESS

1. When an alloy containing lead or tin is dissolved in hot sulfuric acid, there is considerable free sulfur liberated. This does no harm.

2. The alloy must be digested with the sulfuric acid at a boiling heat for several minutes in order to dissolve it completely and to oxidize all the tin to the "ic" form. There is no tendency for the antimony to be oxidized further than to the trivalent state.

3. It is necessary that the lead sulfate be ignited at a dull red heat for some time since it seems to hold excess sulfuric acid very tenaciously. Even then the results tend to run a little high.

4. In the antimony titration it is necessary to employ a large excess of permanganate in order to complete the oxidation. Often the solution will become turbid during the titration, but this does not affect the results. When the titration is made thus, in a solution free from HCl, the end point is not evanescent.

The following are some results obtained by the above method:

Grams Lead		Grams Antimony		Grams Tin		Grams Copper	
Taken	Found	Taken	Found	Taken	Found	Taken	Found
0.600	0.602	0.200	0.200	0.200	0.201	0.0460	0.0450
0.600	0.599	0.200	0.201	0.200	0.201	0.0440	0.0440
0.600	0.602	0.200	0.199	0.1350	0.1340
1.000	1.001	0.200	0.200	0.200	0.200	0.0430	0.0425
0.500	0.502	0.250	0.250	0.250	0.252	0.0890	0.0894
...	...	0.200	0.200	0.200	0.200	0.0500	0.0500
0.700	0.703	0.300	0.301	0.150	0.149	0.2500	0.2510
0.500	0.500	0.250	0.249	0.250	0.250	0.0500	0.0500
0.700	0.701	0.150	0.148	0.0500	0.0490
0.600	0.601	0.200	0.200	0.200	0.200	0.0255	0.0250
0.600	0.600	0.200	0.200	0.200	0.200	0.0255	0.0254
...	0.0255	0.0240
...	0.0255	0.0256

The copper in the above experiments was determined by the sulfocyanate-permanganate method.¹

The purity of the metals used was ascertained by determining the most likely impurities in them. The weights taken in the above experiments were such as to give the amounts recorded.

DEPARTMENT OF METALLURGY
OHIO STATE UNIVERSITY
COLUMBUS

A RAPID AND ACCURATE GRAVIMETRIC METHOD FOR DETERMINING FAT IN ICE CREAMS, CEREALS AND CHOCOLATE

By E. P. HARDING AND GUY PARKIN

Received July 14, 1913

In THIS JOURNAL, 5, 131, the authors of this paper described a method for determining milk-fat in evaporated milk and milk powders at the conclusion of which they stated that the method was at that time being tried out on various ice creams, on cheese, cereals, flours and various other products.

The present paper is a continuation of that work

¹ THIS JOURNAL, 4, 597.

¹ THIS JOURNAL, 5, 218.

and as the amount of the substance used in an analysis, its nature and fat content differ from those of the milk products, the method will be given again somewhat in detail.

A. THE DETERMINATION OF FAT IN ICE CREAM

The reagents used are acetic acid, 25 per cent by volume; carbon tetrachloride, redistilled; 95 per cent ethyl alcohol, redistilled; and redistilled petroleum ether with boiling point 50° C. to 70° C.

The apparatus used is a 100 cc. Nessler jar or any convenient 100 cc. extraction tube with two rubber stoppers, one unperforated and used while shaking, the other doubly perforated carrying blow-off tubes, similar to the Werner-Schmidt blow-off tubes but with a double bulbed rubber air-pressure pump for forcing the ether layer out of the extraction jar. A 11 cm. filter paper, funnel and stand, wide-mouthed flasks of 50 to 75 cc. capacity for weighing the fat, a small evaporating dish for holding wash petroleum ether, a petroleum ether wash bottle, a condenser, and a drying oven.

The process in detail is as follows: The ice cream is melted by warming to 50° C. and well mixed, without churning, to form a uniform sample. Five grams of this mixture are weighed into the 100 cc. extraction jar, 5 cc. of 25 per cent acetic acid added, and the contents warmed to about 50° C. by cautiously rotating the jar over a low flame or by placing it in a water bath at that temperature. When the protein has dissolved, 12 cc. of carbon tetrachloride are added and the jar vigorously shaken for two minutes. Ten cc. of alcohol are added, the jar again vigorously shaken, then 35 cc. of petroleum ether are added and the vigorous shaking continued one minute. The jar is then allowed to stand from one to two minutes when the separation will be complete. (If an emulsion forms it can be broken up with a few drops of alcohol.) The blow-off tube is then inserted and the ether layer cautiously blown onto the filter which filters through onto the tared flask. (In blowing off the ether layer, care must be taken that none of the carbon tetrachloride layer is blown off which may happen if a too close separation of the two layers is attempted. This may be avoided with reasonable care in the manipulation.) Five cc. of carbon tetrachloride are then added to the contents of the jar which is thoroughly shaken, then 30 cc. of petroleum ether are added, the jar again thoroughly shaken, one minute allowed for separation and the ether layer blown off with the necessary precautions as above stated. Another addition of 5 cc. of carbon tetrachloride and 30 cc. of petroleum ether is made with thorough shaking after each addition, and the separation of the ether layer after one minute standing is repeated as in the first blow off. Five cc. of petroleum ether are then placed in the small evaporating dish and gently drawn into the jar by sucking on the blow-off tube; after a few seconds this ether which has mixed with the thin ether layer in the jar is blown off through the filter. The filter paper is then well washed with small portions of petroleum ether, about 15 cc. in all, the flask connected with the condenser, the ether distilled off, and the flask heated for

one hour (to constant weight) at 100° C. in the drying oven, then weighed.

During the process while the jar is being prepared for the second and third blow offs, the weighing flask is connected with the condenser and most of the ether distilled off. This shortens the process to about one and one-half hours and permits the use of a 50 to 75 cc. flask for weighing the fat.

TABLE I. RESULTS SHOWING THAT A FOURTH BLOW OFF IS NOT NECESSARY

Sample No.	1st, 2d and 3d Blow offs		4th Blow off	
	Grams weight	Per cent fat	Grams weight	Per cent fat
I	0.3909	13.03	0.0003	0.01
II	0.3303	11.02	0.0012	0.04
III	0.3378	11.29	0.0009	0.03
IV	0.3601	12.00	0.0003	0.01
V	0.2741	9.14	0.0006	0.02

TABLE II. RESULTS OBTAINED ON VANILLA ICE CREAMS¹

The Rose-Gottlieb Method as given in Circular 66 and the Babcock Method as given in Leach were used as comparison methods.

Sample No.	Harding Parkin			Rose-Gottlieb			Modified Babcock
	Sample weight Grams	Grams fat	Per cent fat	Sample weight Grams	Grams fat	Per cent fat	
389	3.00	0.3375	11.25	3.00	0.3387	11.29	10.00
389	3.00	0.3363	11.21	3.00	0.3312	11.04	10.00
389	3.00	0.3378	11.29				
395	3.00	0.3307	11.02	3.00	0.3303	11.01	10.00
218	3.00	0.3601	12.00	3.00	0.3540	11.80	11.00
218	3.00	0.3612	12.04	3.00	0.3580	11.93	11.00
219	3.00	0.2741	9.14	3.00	0.2755	9.18	8.00
233	3.00	0.2804	9.34	3.00	0.2787	9.29	
231(a)	3.00	0.2897	9.65	3.00	0.2850	9.50	7.00
X	3.00	0.2251	7.50	3.00	0.2250	7.50	6.00
Y	3.00	0.2338	7.79	3.00	0.2261	7.53	
Z	3.00	0.2404	8.01	3.00	0.2350	7.83	
I	3.00	0.2438	8.12	3.00	0.2415	8.05	
II	3.00	0.2493	8.31	3.00	0.2419	8.06	
III	3.00	0.2379	7.99	3.00	0.2394	7.98	

(a) Determination was made on a soured sample.

TABLE III. RESULTS ILLUSTRATING CHANGE IN BUTTER-FAT CONTENTS OF VARIOUS PARTS OF AN ICE-CREAM PACKER AFTER STANDING

The samples were two gallon packers which were well filled and in a fresh frozen condition when first sampled. The second sampling was made after the packer had stood twenty-four hours without disturbing at room temperature.

Sample No.	Fresh frozen condition			After standing 24 hours		
	Top Per cent fat	Middle Per cent fat	Bottom Per cent fat	Top Per cent fat	Middle Per cent fat	Bottom Per cent fat
I	12.17	12.19	12.05	12.38	12.21	12.12
II	12.66	12.34	12.63	12.61	12.57	12.41

CONCLUSION

The method is recommended for determining fat in ice cream because:

I. It is a short, practical gravimetric method readily adapted to commercial control work, requiring from one to one and one-half hours for a complete determination.

II. It gives a pure fat.

III. It gives a larger per cent of fat when compared with standard methods.

¹ See also results obtained on chocolate ice creams, *THIS JOURNAL*, 5, 134.

IV. It will give accurate results without a close adherence to the amounts of reagents used.

B. THE DETERMINATION OF FAT IN CEREALS, COMPOUND CEREALS, FERTILIZERS AND CHOCOLATES

The method used in the determination of oil in cereals, compound cereals and fertilizers with one exception was the same as that applied to ice creams. It was found that acetic acid would not cut the fiber and liberate the oil quantitatively. The same volume of hydrochloric acid with a specific gravity of 1.12 was substituted for the acetic acid with quantitative results.

The method as applied to chocolate was the same as that applied to cereals with the exception that it was necessary to centrifuge two minutes in obtaining the first separation. The following data will show that the Bigelow and Albrech method gives higher results but the extract upon evaporation contained fibrous material which it was impossible to filter off and therefore weighed as oil.

TABLE I—RESULTS OBTAINED ON GRAHAM FLOUR, BUCKWHEAT FLOUR, COMPOUND CEREALS AND FERTILIZERS

The sixteen-hour ether extraction method as given in Food Inspection and Analysis by Leach was used as a comparison method

Sample No	Harding-Parkin			16 hour ether extract		
	Flour Grams	Oil Gram	Per cent	Flour Grams	Oil Gram	Per cent
I.....	2	0.0518	2.59			
I.....	2	0.0521	2.60			
I.....	2	0.0529	2.64			
I.....	2	0.0535	2.67			
II.....	2	0.0422	2.11	2	0.0410	2.05
III.....	2	0.0311	1.56	2	0.0300	1.50
III.....	2	0.0310	1.55			
IV.....	2	0.0492	2.46	2	0.0482	2.41
IV.....	2	0.0476	2.38	2	0.0475	2.37
IV.....	2	0.0505	2.52			
IV.....	2	0.0493	2.46			
IV.....	2	0.0494	2.47			
IV.....	2	0.0490	2.45			
IV.....	2	0.0477	2.38			
IV.....	2	0.0498	2.49			
IV.....	2	0.0510	2.55			
IV.....	2	0.0497	2.48			
V.....	2	0.0490	2.45	2	0.0478	2.39
V.....	2	0.0492	2.46			
VI.....	2	0.0372	1.86	2	0.0385	1.92
VI.....	2	0.0361	1.80			
VII(a).....	2	0.0630	3.15	2	0.0590	2.95
VIII(a).....	2	0.0504	2.52	2	0.0500	2.50
VIII(a).....	2	0.0516	2.58			
IX(a).....	2	0.0540	2.70	2	0.0533	2.66
X(b).....	2	0.0760	3.80	2	0.0774	3.87
X(b).....	2	0.0744	3.72			
X(b).....	2	0.0740	3.70			
XI(c).....	2	0.2128	10.64	2	0.2127	10.63
XI(c).....	2	0.2371	11.85	2	0.3360	11.80

(a) Determination on buckwheat flour.

(b) Determination on compounded cereals.

(c) Determination on fertilizers.

TABLE II

The following data were obtained showing a fourth blow off to be unnecessary.

Sample No	1st, 2d, 3d Blow off		4th Blow off	
	Gram	Oil Per cent	Gram	Oil Per cent
207	0.0422	2.11	0.0012	0.06
203	0.0630	3.15	0.0008	0.04
211	0.0516	2.58	0.0006	0.03

TABLE III

The following results were obtained on chocolate. The Bigelow and Albrech Method as given in the Proceedings of A. C. A. C. Bull. No. 137, pp. 102-3, was used as a comparison method.

Sample No.	Harding-Parkin			Bigelow-Albrech		
	Chocolate Grams	Cocoa Butter Grams	Cocoa Butter Per cent	Chocolate Grams	Cocoa Butter Grams	Cocoa Butter Per cent
173	2.00	1.0393	51.96	2.00	1.0720	53.60 ^a
173	2.00	1.0341	51.70 ^b	2.00	1.0680	53.40 ^a

(a) This cocoa butter had a dirty appearance and contained chocolate fiber.
(b) The refractive index of this fat was found to be 1.4575 at 40°C.

CONCLUSION

I. The method extracts all the oil from cereals and fertilizers and requires but two hours for a complete determination. Other reliable methods require sixteen hours of extraction.

II. It extracts from chocolate all the oil in a pure, fibrous-free condition.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS

PROPOSED METHOD FOR DETECTING ADULTERATION OF CIDER VINEGAR WITH DISTILLED VINEGAR

By S. L. CRAWFORD

Received July 28, 1913

At the present time it is only possible to determine whether a cider vinegar has been adulterated with an appreciable amount of distilled vinegar, providing the different constituents have not been raised to cover up the addition of the distilled vinegar. The glycerine determination, for example, is only valuable providing a sufficient amount of glycerine has not been added to the vinegar to make up for the lowering of the glycerine content caused by the addition of distilled vinegar. Therefore, in looking for a way of determining whether cider vinegar contains added distilled vinegar, our principal aim has been to find some difference between cider vinegar and distilled vinegar, which could not be affected by additions made to the vinegar.

It has been known for some time that there was in cider vinegar a volatile constituent which had a reducing effect on Fehling's solution, and in order to get the true amount of reducing sugars in vinegar, it is necessary to evaporate several times after the addition of water. What this substance is, has not yet been determined, but what we found was that while distilled vinegar or pyroligneous acid does not contain any appreciable amount of this volatile substance, all cider vinegar shows its presence in sufficient amount to make it a valuable constant in determining the purity of a vinegar.

The proposed method is to take 50 cc. of sample, dilute to 250 cc. and distil over 200 cc. into a 250 cc. flask. Neutralize and make up to the mark. Take 50 cc. of this distillate and determine sugars by the method given in Bureau of Chemistry, *Bulletin* 107. The result is given as invert sugar according to Munson and Walker's tables.

In Table I are shown results determined on seven

different samples of distilled vinegar obtained from different sources, and of varying age running from one month to one year. It will be seen from the figures given in Table I that distilled vinegar when reduced to 4 per cent acid strength contains from a trace to 0.0026 gram per 100 cc. of this volatile substance, which is practically negligible.

In Table II is given the amount found in a fully fermented dry refined cider six months old, and a completely fermented first pressing juice, which has not been refined, also six months old. As only traces were found in these samples, it goes to show that the volatile substance is produced during the acetification of the apple juice.

Table III shows the amount found in four samples of cider vinegar made from first pressings, having an average of 0.162 gram on a 4 per cent basis.

TABLE I

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent basis
1	Distilled vinegar....	10.0	0.0065	0.0026
2	Distilled vinegar....	9.44	Trace	Trace
3	Distilled vinegar....	10.67	Trace	Trace
4	Distilled vinegar....	9.01	0.0005	0.0002
5	Distilled vinegar....	10.46	0.0048	0.0017
6	Distilled vinegar....	9.61	0.0010	0.0004
7	Distilled vinegar....	10.38	Trace	Trace

TABLE II

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.
8	Dry refined cider	0.36	Trace
9	1st pressing	0.75	Trace

TABLE III

Sample	Composition	Acid. Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
10	1st press.....	4.70	0.2232	0.190
11	1st press.....	4.70	0.2051	0.174
12	1st press.....	4.50	0.1664	0.148
13	1st press.....	4.20	0.1424	0.136

TABLE IV

Sample	Composition	Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
14	2nd press.....	5.53	0.2244	0.162
15	2nd press.....	4.62	0.2092	0.181
16	2nd press.....	4.20	0.1784	0.170

TABLE V

Sample	Percentage composition		Acid Grams 100 cc.	Vol. red. substance Grams 100 cc.	Red. to 4 per cent acid basis
	1st press	2d press			
17.....	75	25	4.98	0.1824	0.147
18.....	66.7	33.3	4.48	0.1405	0.125
19.....	75	25	4.72	0.1752	0.149
20.....	75	25	4.86	0.1621	0.133
21.....	85	15	4.96	0.1384	0.111
22.....	66.7	33.3	4.72	0.1562	0.133
23.....	75	25	4.82	0.1520	0.126
24.....	50	50	5.52	0.1700	0.123
25.....	50	50	5.69	0.1840	0.129

In Table IV are the amounts found in three samples of cider vinegar made from second pressings, all kept different lengths of time before repressing. Sample No. 14 was repressed the second time one hour after the first pressing; No. 15 nineteen hours after the first pressing; and No. 16 was repressed five days after the first pressing.

As these figures are fairly constant, it does not appear to make any appreciable difference in the amount of volatile reducing substance present, how long the pomace is kept before repressing.

Table V shows nine samples of cider vinegar composed of varying amounts of first and second pressings, and it will be seen that the amount of volatile substance found is fairly constant when reduced to a 4 per cent basis, running from 0.111 to 0.149.

All of the above samples are of known purity and all comparatively new vinegars, none of them being more than one year old.

While the above figures are not sufficient evidence upon which to determine the purity of a cider vinegar, it would seem from the work done, that if a large number of vinegars of varying composition and age were examined, a maximum or minimum content for cider vinegar could be found, which would, in addition to the known glycerine content and other constants, be of considerable aid in determining whether a cider vinegar has been adulterated with distilled vinegar or pyroligneous acid.

If desired, it can be readily determined whether the adulteration is due to the presence of distilled vinegar or pyroligneous acid, owing to the fact that if pyroligneous acid has been used, the vinegar will contain more than 0.007 gram per 100 cc. of formic acid, while if distilled vinegar has been used, the amount of formic acid present will be below 0.007 gram per 100 cc., depending upon the amount of cider vinegar present in the mixture. A pure cider vinegar when subjected to the formic acid test will show from a trace to 0.007 gram per 100 cc. of a substance which is calculated in this determination as formic acid.

We give below the analysis of a vinegar actually made from distillery slop and distilled vinegar. It will be seen that if this vinegar was branded "reduced with water" to take care of the low non-sugars and ash, it would be impossible for any chemist to prove that it was not a pure cider vinegar.

Specific gravity at 20° C.....	1.0145
Acetic acid, grams per 100 cc.....	4.86
Solids, grams per 100 cc.....	1.97
Reducing sugars before inversion, grams per 100 cc.....	0.70
Ash, grams per 100 cc.....	0.209
Alkalinity of ash, cc. N/10 acid.....	29.60
Phosphoric acid soluble, mgms. per 100 cc.....	6.98
Phosphoric acid insoluble, mgms. per 100 cc.....	17.38
Polarization degrees Ventzke.....	-1.6
Formic acid, grams per 100 cc.....	Absent
Glycerine, grams per 100 cc.....	0.292
Volatile reducing substance, grams per 100 cc.....	Absent
Lead precipitate.....	Good
Artificial color.....	None detected
Non-sugars, grams per 100 cc.....	1.27
Per cent of solids reducing sugars.....	35.50
Ratio of ash to non-sugars.....	1.6

One form of adulteration which the above method would be useful in detecting is when the slop or residue from an apple brandy still is mixed with a weak solution of alcohol and run over the generators, or distilled vinegar is added direct, artificially colored and sold as cider vinegar.

As practically every constituent of the apple is left unchanged in the still after distillation, it is almost

impossible to detect this form of adulteration by any of the regular methods of analysis, for nothing has been taken away from the original apple juice except the alcohol, and that is replaced either with other alcohol or its equivalent of acetic acid. A vinegar of this kind, however, contains either no volatile reducing substance or only a trace, due to the small amount present in the distilled vinegar, as the original apple juice has never undergone the acetic fermentation, at which stage the volatile reducing substance is formed. For this reason the adulteration can be readily detected.

NATIONAL FOOD MANUFACTURERS' LABORATORY
ROCHESTER, NEW YORK

CHEMICAL STUDIES ON THE LIME SULFUR-LEAD ARSENATE SPRAY MIXTURE

By W. E. RUTH

Received July 14, 1913

PREVIOUS WORK

Much experimental work has been done with arsenicals of various kinds in the way of spraying tests and methods of preparation; most of this, however, has been carried on by horticulturalists and entomologists. Some work has been done with lime sulfur, with a view to methods of preparation and the forms of combination in which the sulfur is present in solution. More of the latter work has been performed by chemists.

As far as known at present, Bradley¹ and Tartar² have made the only studies of lime sulfur and lead arsenate mixtures from a chemical standpoint. Their work consisted of comparing the neutral with the acid lead arsenate when mixed with lime sulfur. They compared the total sulfur and calcium content of the lime sulfur but made no study of the various forms of sulfur in solution before and after mixing.

EXPERIMENTAL

COLOR CHANGES.—To every one who has handled lime sulfur and lead arsenate in a mixture for one spraying, it is a well known fact that a change occurs in the appearance of lead arsenate. The white lead arsenate very soon becomes black in presence of lime sulfur solution. If a solution of lead acetate be added to a solution of sodium thioarsenate a precipitate when first formed has a reddish yellow color which very soon gives way to a darker brown and this in turn to a very dark gray—almost black.

Several drops of concentrated lime sulfur solution added to a small quantity of fine particles of lead arsenate suspended in water will result in the lead arsenate undergoing the same color changes described above in the precipitation of the lead thioarsenate. With the addition of the first lime sulfur solution the particles of lead arsenate turn to the reddish yellow color and in the presence of more lime sulfur it turns darker and finally black in the excess of lime sulfur.

Again if the lime sulfur be added to the lead arsenate in the water in small diluted portions, up to a certain point the sulfur will be precipitated so as to decolorize completely the solution and beyond that point the color of further additions of lime sulfur apparently is not affected.

¹ THIS JOURNAL, 1, 606.

² *Ibid.*, 2, 271, 328.

EFFECT ON LEAD ARSENATE OF MIXING WITH LIME SULFUR SOLUTION

At first it was attempted to mix small definite quantities of lead arsenate with accurately measured portions of lime sulfur solution so that definite quantities of lead and arsenate could be accounted for after mixing with lime sulfur. This, however, was abandoned, because it was found impractical to separate the black lead-arsenate-sulfur residue quantitatively from the filter upon which it was separated and washed from the lime sulfur.

To avoid this difficulty, quantities of approximately one hundred grams of lead arsenate were mixed with lime sulfur. (Lime sulfur concentrate 32.5° B., diluted 1 to 40, about the concentration recommended for summer spray.) The mixture was prepared from Grasselli commercial lime sulfur and Sherwin Williams "New Process" lead arsenate which was slightly acid to litmus. The latter showed the following analysis, dry basis:

Total lead (Pb) Per cent	Total arsenic oxide oxide (As ₂ O ₃) Per cent	Water-soluble As ₂ O ₃ Per cent
64.18	26.42	0.42
64.28	26.52	0.46

The lime sulfur was used in large excess in an attempt to simulate conditions that obtain in spraying. The mixture was very frequently stirred to prevent the caking that is so common with lead arsenate in lime sulfur. After standing several hours the lead-arsenic-sulfur residue was filtered with suction and washed with previously boiled and cooled water to the complete disappearance of color of lime sulfur solution, and then with several hundred cc. more of water to insure complete removal of lime sulfur. The residue was dried in an oven not over 40° C. and kept in a vacuum desiccator until ready for analysis.

One-gram samples were digested with 100 cc. of approximately 10 per cent nitric acid solution on the steam bath for several hours; filtered, washed and the digestion repeated. The solution contained the lead arsenic and calcium. It was transferred to a 300 cc. volumetric flask, diluted to the mark and aliquots used for determining the lead and arsenic. The lead was determined from the solution by the chromate method and the arsenic by the modified Gooch and Browning method.

One preparation of the mixture gave the following results for lead and arsenic oxide:

	Lead (Pb) Per cent	Arsenic oxide (As ₂ O ₃) Per cent
1.....	42.61	8.87
2.....	42.17	9.06
3.....	42.24	8.86
4.....	42.28	8.89

A second preparation gave the following by the same method:

	Lead (Pb) Per cent	Arsenic oxide (As ₂ O ₃) Per cent
1.....	45.52	9.09
2.....	45.72	9.09

The total sulfur, free sulfur and calcium were also

determined in the second preparation, showing the following:

	Total sulfur Per cent	Free sulfur Per cent	Total calcium Per cent
1	22.51	19.32	5.14
2	22.52	19.56	5.02

Total sulfur was determined by the Fresenius¹ method, the arsenic being removed from the hydrochloric acid solution with H_2S . The calcium was determined by the Rose² method of decomposition with chlorine and separation of lead and arsenic by hydrogen sulfide. Free sulfur was determined by carbon disulfide extraction.

The decrease in percentages of lead and arsenic from those of the original lead arsenate to the percentages in the mixture is very marked. The decrease is apparently due to the addition of sulfur and calcium to the mixture. But the results of analyses do not total a hundred per cent, as shown below:

Pb	45.62
Total S.	22.51
Ca	5.08
As 2O_3	9.09
	82.30

This evident loss caused the writer to try some method of examining the mixture for the presence of oxygen compounds of sulfur such as sulfates, sulfites or thiosulfates. Accordingly, one-gram samples were placed in the shaker bottles with about 800 cc. of previously boiled and cooled distilled water, shaken for four hours and filtered. These solutions were made up in liter flasks and aliquots used in analyses. Solutions gave strong tests for calcium with ammonium oxalate, as well as a test for thiosulfate, but no evidence of sulfide, sulfites or sulfates.

The solutions decolorized iodine solution but when bleached again with stannous chloride gave no precipitates with barium chloride in hydrochloric acid solution (even after long standing), thus eliminating presence of sulfites or sulfates. A portion of the solution boiled with hydrochloric acid became cloudy in appearance, due to free sulfur precipitating from the decomposition of thiosulfate. Other portions of the solutions mixed with chlorine water and allowed to stand over night, then boiled and acidified with hydrochloric acid, gave liberal precipitates of barium sulfate indicating the thiosulfate.

Quantitative determinations of sulfur by the latter described method and calculated for the whole solutions gave the following results:

No.	Free sulfur Gram	Calculated equivalent of CaS_2O_3 Gram
1	0.0188	0.03324
2	0.0185	0.04255
3	0.0176	0.04048
4	0.0194	0.04462
5	0.0162	0.03726
6	0.0159	0.03657
7	0.0162	0.03726
8	0.0172	0.03956

The amounts of calcium thiosulfate shown here

calculated to the original weight of the sample show from three and three-tenths to four and four-tenths per cent thiosulfate present. The solutions showed only traces of arsenic, so that very small quantities of calcium arsenate could possibly be present.

The Cornell Station¹ has shown that mixing lead arsenate with lime sulfur increases the fungicidal value of lime sulfur. Haywood² in his work on lime sulfur says: "It is a well known fact that sulfites act as anti-septic agents. There is reason to believe that they would also act as insecticides. From the decomposition of the wash there are obtained sulfur in a very finely divided form, thiosulfate for a time, and sulfite which is gradually set free. The writer (Haywood) is of the opinion that these are the active agents in killing insects." Haywood shows by reaction how the thiosulfates are formed from the polysulfides. If it is true, as he supposes, that the fungicidal properties of lime sulfur are largely due to the formation of thiosulfates and sulfites with liberation of free sulfur, here then is an explanation, partially at least, for the increase of the fungicidal properties of the lime sulfur solution when mixed with lead arsenate.

Bradley and Tartar³ state that no sulfides of arsenic are formed since they would be soluble in the alkaline lime sulfur solution, but none were found in the solution. The writer also failed to find any sulfide of arsenic in the lime-sulfur solution.

If a portion of the lead arsenate-sulfur residue be covered with a 10 per cent sodium hydroxide solution, then warmed on the steam bath for a short time and allowed to settle, some of the supernatant liquid when acidified with hydrochloric acid will be shown to contain arsenic sulfide. A small quantity will be thrown out of solution. A part of the residue remaining after extraction for free sulfur was treated with the alkali, but the solution gave no precipitate of arsenic sulfide when acidified.

A second portion of the residue which had been extracted until free from sulfur was warmed with sodium polysulfide. After standing several hours on the steam bath the liquid gave quite a heavy precipitate of arsenic sulfide when acidified with hydrochloric acid. Arsenic in the arsenic sulfide precipitates was verified by boiling with hydrochloric acid and potassium chlorate and precipitating as magnesium ammonium arsenate.

EFFECT OF MIXING ON LIME SULFUR

To observe the effect of mixing on the lime sulfur solution approximately one-gram samples of the lead arsenate dried free from moisture were mixed with accurately measured quantities of the lime sulfur solution (concentrate 32.5° B. used in different dilutions). The mixtures were made in small ground glass stoppered flasks that were filled by the quantities of lime sulfur used so as to exclude all air possible. The lime sulfur was separated from the lead arsenate residues by means of Gooch filters. Aliquot parts of 10 cc. were immediately drawn off, and the de-

¹ Wallace, Blodgett and Hesler, Cornell Sta., *Bull.* 290.

² Haywood, Bureau of Chem., U. S. D. A., *Bull.* 101.

³ *Loc. cit.*

¹ Treadwell and Hall, p. 357, Vol. II, 3rd ed.

² *Ibid.*, p. 359.

termination of total sulfur made from one, and total sulfides, thiosulfate, sulfite and sulfate all made from a second part.

The monosulfide sulfur was not determined but total sulfide sulfur was precipitated by iodine solution, determined as barium sulfate and the iodine titration continued for thiosulfate as described by Harris.¹

As comparative results were sought in the lime sulfur before and after mixing with lead arsenate the above method was found very satisfactory and quick for precipitating the sulfide sulfur.

After the thiosulfate titration the sulfide sulfur was filtered off, and sulfites, now oxidized to sulfates, along with any sulfates originally present, were precipitated as barium sulfate in the cold hydrochloric acid solution by standing at least twelve hours.

The results of analyses of lime sulfur mixed with lead arsenate as described above are shown below in Tables I and III. Those shown in Table I are for mixtures standing one hour and Table III shows results for mixtures standing overnight. Tables II and IV show the differences in the various forms of sulfur, being more or less, as the case may be, than in the original lime sulfur solution before mixing with lead arsenate.

Tables II and IV show losses of sulfide sulfur and calcium from solutions and increases of thiosulfate and sulfate (including sulfites) in every case. Mixtures Nos. 1, 2, 3, in both Tables I and III were made at the same time from the same diluted lime sulfur solution with approximately the same weights of lead arsenate as shown in the tables. The results in the first three mixtures, Table I, show that the thiosulfate in solution is increased in the lime sulfur by mixing as well as the sulfate (including sulfites), but upon further examination of 1, 2, 3, Table III, it will be seen that the oxidation has continued—the thiosulfates having decreased and sulfates increased. It must be borne in mind that the flasks were full to exclusion of air, and any oxidation could come only from the lead arsenate, also that the water used in dilution of lime sulfur concentrate had been previously boiled to free it from air and carbon dioxide.

Nos. 5 to 14, Table III, are mixtures made with smaller quantities of a more diluted lime sulfur to observe, if possible, the effect of lesser concentration on the mixture. In Table IV it will be noticed that the amount of sulfide sulfur lost from the weaker solution approaches very closely the amount lost from solution in the more concentrated form. The sulfide sulfur loss is due to precipitation in some form by the lead arsenate as well as the formation of thiosulfates and sulfates from the sulfides.

The loss of calcium from the solution apparently is due to only partial solubility of the calcium thiosulfate in the lime sulfur, as well as due to any small quantities of calcium arsenate that may be formed, the latter being mostly insoluble in the excess of lime sulfur solution.

In columns 4 and 5, Tables I and III, are given the total sulfurs in the lime sulfur solutions. The total

TABLE I—ANALYSES OF LIME SULFUR SOLUTION WITH LEAD ARSENATE STANDING ONE HOUR. WEIGHTS OF VARIOUS FORMS OF SULFUR IN GRAMS

No.	1	2	3	4	5	6	7
	Sulfide S	Sulfate S	Thiosulfate S	Total S calculated	Total S determined	Weight of lead arsenate used	Weight of Ca in sol.
1...	0.31200	0.00281	0.03477	0.34958	0.32964	1.0006	0.09539
2...	0.30066	0.00309	0.03635	0.34010	0.32031	0.9997	0.09333
3...	0.29922	0.00295	0.03635	0.33852	0.32243	1.0013	Lost
Blank (a)							
4...	0.42132	0.00116	0.01738	0.43986	0.43735	None	0.12116
5...	0.23245	0.00178	0.03984	0.27407	0.24525	0.0128	0.07817
6...	0.20834	0.00178	0.03824	0.24836	0.22105	1.0015	0.08141
7...	0.21020	0.00178	0.03984	0.25182	0.22222	1.0013	0.07434
8...	0.20607	0.00175	0.03984	0.24766	0.22002	0.9996	0.07640
9...	0.21844	0.00179	0.03984	0.25907	0.23478	1.0203	0.07537
10...	0.21246	0.00178	0.03824	0.25248	0.22846	1.0088	0.07611
Blank (a)							
11...	0.38680	0.00104	0.02231	0.41015	0.38859	None	0.11791

(a) The "blank" determination before mixing is for the same quantity of the same lime sulfur solution used in the mixtures given immediately above.

TABLE II—DIFFERENCES IN GRAMS IN TABLE I FOR WHOLE AMOUNT OF LIME SULFUR USED BEFORE AND AFTER MIXING (1 HOUR)

No.	1	2	3	4	5	6
	Sulfide S Loss	Sulfate S Gain	Thiosulfate S Gain	Difference between total S determined and total S calculated. Gain	Weight of lead arsenate used	Ca loss from solution
1.....	0.10932	0.00165	0.01739	0.01994	1.0006	0.02577
2.....	0.12066	0.00193	0.01897	0.01979	0.9997	0.02783
3.....	0.12210	0.00179	0.01897	0.01609	1.0013	Lost
5.....	0.15435	0.00074	0.01753	0.02882	1.0128	0.03974
6.....	0.17846	0.00074	0.01593	0.02731	1.0015	0.03650
7.....	0.17660	0.00074	0.01753	0.02960	1.0013	0.04357
8.....	0.18073	0.00071	0.01753	0.02764	0.9996	0.04151
9.....	0.16836	0.00075	0.01753	0.02429	1.0203	0.04254
10.....	0.17434	0.00074	0.01593	0.02402	1.0088	0.04180

TABLE III—ANALYSES OF LIME SULFUR SOLUTION WITH LEAD ARSENATE STANDING OVERNIGHT. WEIGHTS OF VARIOUS FORMS OF SULFUR IN GRAMS

No.	1	2	3	4	5	6	7
	Sulfide S	Sulfate S	Thiosulfate S	Total S calculated	Total S determined	Weight of lead arsenate used	Ca in solution
1...	0.21782	0.00350	0.02687	0.24819	0.25052	1.0024	0.07537
2...	0.21391	0.00419	0.02529	0.24339	0.23925	1.0017	0.07493
3...	0.23390	0.00391	0.02055	0.25836	0.26198	1.0021	0.08067
Blank (a)							
4...	0.42132	0.00116	0.01738	0.43986	0.43735	None	0.12116
5...	0.0364	0.0024	0.0231	0.0619	0.0797	0.0125	...
6...	0.0362	0.0020	0.0231	0.0613	0.0770	0.0194	...
7...	0.0352	0.0022	0.0245	0.0619	0.0782	0.0122	...
8...	0.0352	0.0021	0.0191	0.0564	0.0669	0.0065	...
Blank (a)							
9...	0.2162	0.0010	0.0137	0.2299	0.2269	None	...
10...	0.0607	0.0031	0.0167	0.0805	0.0860	1.0007	...
11...	0.0688	0.0029	0.0175	0.0892	0.0946	0.9994	...
12...	0.0739	0.0031	0.0159	0.0929	0.0969	1.0072	...
13...	0.0648	0.0032	0.0159	0.0839	0.0917	1.0289	...
Blank (a)							
14...	0.2448	0.0010	0.0155	0.2613	0.2680	None	...

(a) The "blank" determination before mixing is for the same quantity of the same lime sulfur solution used in the mixtures given immediately above.

sulfur as calculated (shown in column 4) is found by summing up the three forms of sulfur in solution.

The total sulfur shown in column 5 is that determined directly on a separate portion of the solutions. Columns

¹ Mich. Sta., Tech., Bull. 6.

4, Tables II and IV, show the differences between the two results for total sulfur.

The difference shown in Table II is indicated as a gain, that is, the calculated total shows a gain when compared with total sulfur by determination. This difference was at first thought to be due to analytical error but when the same comparisons were made for the mixtures standing overnight, with only one exception as indicated, the calculated totals show a loss as compared with the total sulfur as determined direct.

TABLE IV DIFFERENCES IN GRAMS IN TABLE III FOR THE WHOLE AMOUNT OF LIME SULFUR USED BEFORE AND AFTER MIXING (12 HOURS OR MORE)

No.	1 Sulfide S Loss	2 Sulfate S Gain	3 Thiosulfate S Gain	4 Difference between to- tal S deter- mined and total S cal- culated Loss	5 Weight of lead arsenate	6 Ca loss from solution
1...	0.20350	0.00234	0.00949	0.0033	1.0024	0.04579
2...	0.20741	0.00303	0.00791	0.00414(a)	1.0017	0.04623
3...	0.18742	0.00275	0.00317	0.00362	1.0021	0.04049
5...	0.1798	0.0014	0.0104	0.0178—	1.0125
6...	0.1800	0.0010	0.0104	0.0157	1.0194
7...	0.1810	0.0012	0.0118	0.0163	1.0122
8...	0.1810	0.0011	0.0064	0.0105	1.0065
10...	0.1841	0.0021	0.0012	0.0055	1.0007
11...	0.1760	0.0019	0.0020	0.0054	0.9994
12...	0.1709	0.0021	0.0004	0.0040	1.0072
13...	0.1800	0.0022	0.0004	0.0078	1.0289

(a) No. 2 is the only exception in the table where the total sulfur as calculated by summing up the three forms of sulfur showed a gain over the total sulfur as determined.

Whether the gain as shown by the calculated total at the end of an hour is due to analytical error and the loss shown by the calculated total of mixtures after long standing is due to formation of a form of sulfur not included by the present analytical methods, or whether they are both due to analytical error, is not understood and no explanation is offered for it at this time.

DISCUSSION OF RESULTS

As stated before, the writer failed to find any arsenic sulfide in the lime sulfur. But the evidence presented leads the writer to believe that a small amount of the arsenic oxide is converted into the sulfide or that it forms a thioarsenate possibly with lead which would hold it insoluble in the weaker alkaline lime sulfur solution. The close analogy of the color changes undergone by precipitating lead thioarsenate and that of mixing lead arsenate and lime sulfur led the writer to look for the formation of arsenic sulfide.

The results show that the mixing of lead arsenate and lime sulfur increases the thiosulfates and sulfites in the residue. If Haywood¹ is correct in his view that the fungicidal value of lime sulfur is due to the presence

of thiosulfate and sulfites, this increase of thiosulfate in lime sulfur upon mixing it with lead arsenate probably explains the increased fungicidal value of the lime sulfur and lead arsenate mixture.

In conclusion, the writer wishes to acknowledge his indebtedness to Dr. A. W. Dox, of this Station, at whose instigation the above work was undertaken.

AGRICULTURAL EXPERIMENT STATION
IOWA STATE COLLEGE
AMES

SPONGES AS A FERTILIZER

By JOSEPH G. SMITH

Received Aug. 13, 1913

Loggerhead sponge is used with "wonderful results" by the farmers of the Florida Keys who "hardly ever use chemical fertilizers" and it "grows in countless thousands in shallow water where it is easy to procure" as well as to "an enormous size," according to Mr. Thomas E. Reedy of Key West. Its use for the same purpose by the citrus fruit growers of the mainland is attested by Dr. H. F. Moore, of the U. S. Bureau of Fisheries, and has been seen by him growing in such quantities in the salt waters of southern Florida that he has "long thought it should be exploited."

The claims for it as a fertilizer are verified by analyses of samples from Key West submitted by Mr. Reedy, the approximate results on air-dry material being 4 per cent of nitrogen, $\frac{3}{4}$ of 1 per cent each of potash (K_2O) and phosphoric acid (P_2O_5), 5 per cent of lime ($CaOMgO$, mainly CaO) and 40 per cent organic matter. Mr. T. C. Trescott, Chief of the Nitrogen Division of the Bureau of Chemistry, very kindly made the nitrogen determinations. Mr. C. F. Miller, of this Bureau, made the others, duplicating them by repetition, and they were verified in part by the writer.

Analyses of other non-commercial species and of other samples of the Loggerhead are desirable although it is not likely that they differ materially from one another in composition since they all have the same general characteristics and are developed under practically identical conditions.

It is evident from the composition of this material and from its demonstrated efficiency as a fertilizer that it has considerable value to coast and island farmers and fruit growers having easy access to it wherever it is found.

With a view to determining the feasibility of extending its use, further investigations are in progress and contemplated.

BUREAU OF SOILS
DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

LABORATORY AND PLANT

THE CHEMICAL LABORATORY OF THE PICHER LEAD CO.

By JOHN A. SCHAEFFER

Received August 18, 1913

The completion of the new chemical laboratory of

¹ Loc. cit.

the Picher Lead Company, located at Joplin, Missouri, marks another advance in the construction of industrial laboratories, again showing the value of the highest type of equipment for scientific investigation which is so essential in the control of manufacturing opera-

tions, in the study of new processes and in the research work which must necessarily be conducted along all lines in which the manufactured products are utilized. The many new features incorporated in this laboratory will be of undoubted value to chemists and chemical engineers and a description of the laboratory is given with the hope that some points in it may be of ultimate value in the construction and equipment of other industrial laboratories.

The laboratory was so designed and equipped as to fully take care of the varied work which arises in the manufacture of lead and its products. This work embraces constant analytical attention from the ore, Galena, through the smelting processes, the refining processes and thence through the various operations which lead to the finished products. It demands accurate data relative to the formulation of charges based upon analysis, correct furnace temperatures, close study of by-products and continual supervision of furnace practice. Coupled with this is the extensive

fine particles of lead compounds. The usual laboratory equipment is found here—such as apparatus for electrochemical work, electric hot plates, electric furnaces, drying ovens, cupellation muffles and hoods. All



VIEW OF RESEARCH LABORATORY SHOWING LIBRARY AND PHOTOMICROGRAPHIC ROOM

the tables, not only in this room but throughout the building, are equipped with electricity, gas, air, water and drains.

Adjoining the general laboratory is the balance room. Here are found the analytical balances, assay balances and Westphal balance. Concrete piers sunk into the ground, and entirely separate from the building, form the base for the balances and tables. By this means no vibration from the building affects the tables, and this arrangement has resulted in showing only the very slightest vibrations in the balances themselves.

The supply room also connects directly with the general laboratory. This room is so arranged that all heavy reagents are made to syphon directly into closed containers placed upon the table in the general laboratory, thus affording a continual supply of chemicals in the general laboratory itself from the supply room, without the presence of carboys, and with no further attention or entrance into the supply room,



A PORTION OF THE ANALYTICAL LABORATORY

research work which must be carried out on storage batteries, glass, ceramics, enamels, varnishes, rubber and paints, together with the investigation of manufacturing problems which continually arise. The scope of the work along these lines is wide and every effort was made to meet these conditions in the construction and equipment of the chemical laboratory.

The building is a two-story brick and concrete structure—fireproof in every detail, the upper floor being devoted exclusively to research work. The general plan of the laboratory can be well understood by an examination of the accompanying sketches.

The general laboratory, which is devoted to routine work, is located on the ground floor with an eastern and southern exposure so that the best light for volumetric analysis may be obtained. This room, 30 by 32 feet in size, is sufficiently large to accommodate a full corps of chemists. The laboratory tables are of the highest type of construction, consisting of a steel shell resting upon a wood understructure. Into this steel shell a table of vitrified tile was built upon cement, being painted with white cement. The result is a white, durable, unattackable, easily cleaned laboratory table showing any trace of dust, which, in a laboratory dealing with lead products, frequently contains

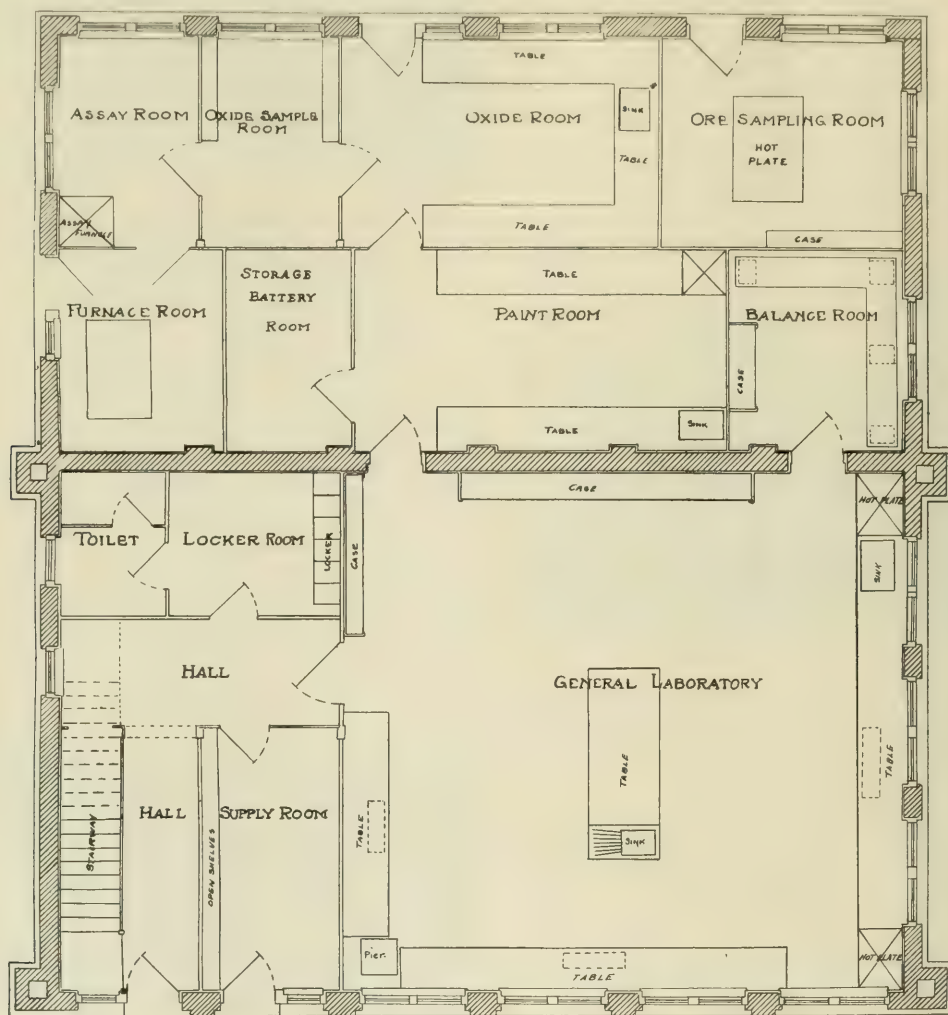
than that which is required for the starting of the syphons when the supply in the carboys is exhausted and new ones are set in place. An unusual saving of time, space and labor has been effected by this arrangement.

The paint room occupies the center of the ground floor. All work on the study of paints, varnishes, enamels and paint compounds is carried out here.

The room is equipped with a laboratory paint mill and mixers, electrically operated. All facilities for the striking of color batches, the grinding of experimental mixes of paints and the manufacture of varnishes have been made.

Ample opportunity for the study of storage batteries and their oxides has been given by the construction of a room devoted solely to this work. This has been so designed that constant temperatures within very

basis, both as regards moisture and metallic content, it is advantageous that this department be separate from the rest of the building. In consequence, the room is not in direct communication with the laboratory and care is exercised that nothing except ore samples reaches this portion of the building. The room is electrically equipped for the grinding and preparation of samples for analysis and contains a large hot plate so designed as to permit of constant temperatures



GROUND FLOOR PLAN

narrow limits can be maintained throughout the entire year. This is of essential importance in the making of life tests on storage batteries. Here all storage battery pastes can be made, grids formed, batteries set up and life tests conducted under ideal conditions.

The ore sampling room, which plays a most important part not only in the purchasing of ores but also in the formulation of charges, occupies one corner of the rear of the building. As all ore is purchased upon an assay

being maintained for the drying of samples preparatory to grinding.

An oxide room is found in the central portion of the rear of the building. This department is a unique feature in the laboratory connected with a plant manufacturing lead products as here each barrel of oxide, either red lead or litharge, is analyzed and its history recorded for future reference. At the same time each sample is matched for color and strength, owing to

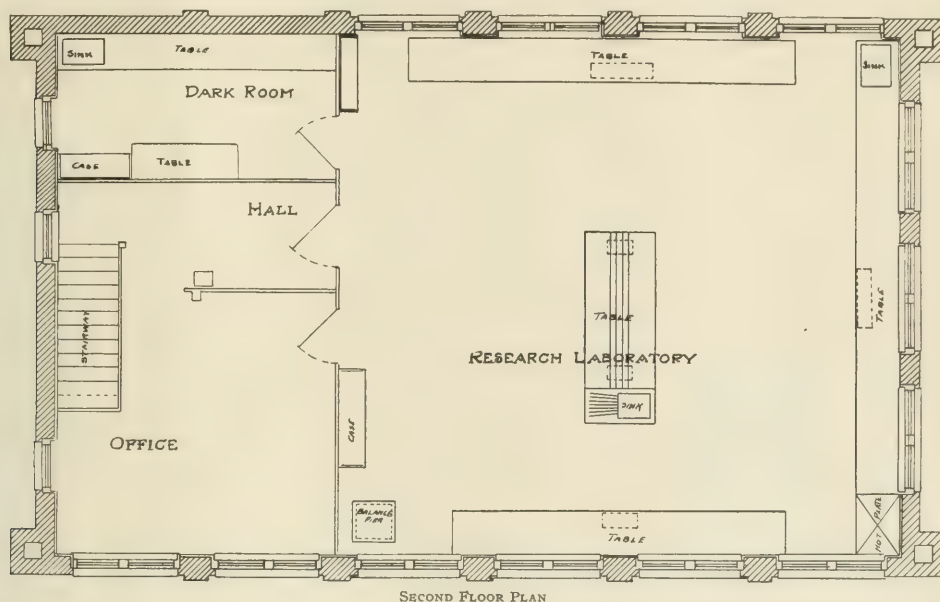
the many varying degrees of shade which are demanded by the trade in these products. Here are found electric stirring devices, balances, facilities for volumetric analysis and the matching of colors. Adjoining the oxide room is the sample room where samples of raw material, fuel and fluxes used in the formulation of charges, by-products and the finished products are carefully tabulated.

The assay room, equipped with muffle furnaces for the determination of gold and silver values in ores and

essential requirements for the development of negatives.

The walls throughout all the building have been plastered and painted with white laboratory enamel unaffected by gases, giving a surface easily washed and of maximum light.

The lighting system has been specially designed by the General Electric Company, the tungsten method of lighting being adopted. The heating of the building is effected by the hot water system.



finished products, completes the plan of the ground floor. It will be seen that every facility for general routine work in the examination of lead and its compounds has been given by the above plan.

On the second floor, devoted exclusively to research work, are found the research laboratory, the office, library and photomicrographic room.

The research laboratory is fully equipped for investigation work on glass, rubber, paints, varnishes, and the study of new processes together with manufacturing problems. Standard equipment of modern types is available for the investigation of any new practice on a scale which will permit of the establishment of data capable of being used directly on a commercial basis. Ample facilities are provided for the study of oils by the use of the viscosimeter and refractometer, together with the examination of the many different compounds through the spectroscope. The most improved methods for the testing of white paints for color and strength have also been installed.

The photomicrographic and microscopic study of paint films and dry pigments, which has of late years become of such importance, is fully provided for in the dark room equipped with low and high power microscopes, photomicrographic apparatus and all

The erection and equipment of this laboratory, complete in every detail, is only another instance of the stress which is laid upon research work and routine work, leading to the accurate control of manufacturing processes by the present-day manufacturer.

JOPLIN, MO.

A SIMPLE GASOLINE GAS GENERATOR FOR SULFUR DETERMINATIONS¹

By C. E. WATERS

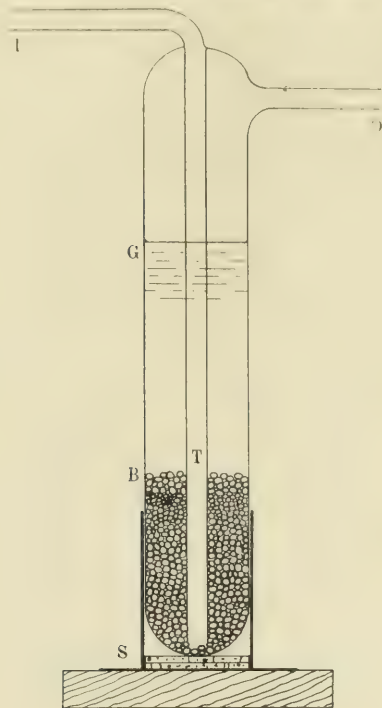
Received August 7, 1913

One of the recognized sources of error in the determination of sulfur as barium sulfate is the taking up of sulfur dioxide and trioxide from the products of combustion of the gas flame. The writer has repeatedly noticed drops of fairly strong sulfuric acid on the underside of platinum dishes in which solutions have been heated for a few hours by a gas flame an inch or so in height. On one occasion a watch glass filled with water was placed over the mouth of a 2-liter flask containing water. After heating over a gas flame for a comparatively short time, the water in the watch-glass gave a turbidity with barium chloride. It has also been found that the dark deposit, commonly regarded as soot, which is found on the bottom of a flask heated on iron gauze, contains a sulfide which

¹ Published by permission of the Director of the Bureau of Standards

at once dissolves in dilute hydrochloric acid with evolution of hydrogen sulfide.

The amount of sulfur that would be absorbed by a solution in a covered beaker during the precipitation of barium sulfate cannot be very large and may be



negligible, but this possible source of error should be eliminated in careful work. Ordinarily solutions to which barium chloride is to be added can be heated most rapidly and conveniently on the steam bath, and only a few minutes' heating over the flame is necessary to bring them to the boiling point. If, however, a fusion is required to transform the sulfur into a soluble sulfate, and especially if the melt must be stirred, the danger of contamination becomes serious. Placing the crucible in a hole in an inclined plate of asbestos board may prevent access of gases from the flame, but there is always danger that particles of gypsum from the board may get into the melt.

An ordinary alcohol lamp gives a flame which is too easily disturbed by drafts and which is not easily regulated. Barthel and other lamps depending on the Bunsen principle are also not satisfactory when a

small flame is needed at the early stages of the fusion. To avoid these difficulties in determining sulfur in rubber, the writer some three or four years ago devised a simple and safe generator for gasoline gas, which is shown in the accompanying sketch.

The large glass tube, 4.5 to 5.0 cm. in diameter, and 25 cm. high, has fused into it the tube I for the admission of compressed air, which is carried down nearly to the bottom through T. It then bubbles up through the layer of beads B, and passes out at O, surcharged with the vapors of petroleum ether or of gasoline, with which the large tube is filled up to the level G. From O the mixture of air and vapor passes through a black rubber tube to the burner. The compressed air, at a pressure of about one meter of water, is also led through black rubber tubing, which cannot cause contamination with sulfur. The object of the beads is to break the stream of air up into innumerable small bubbles, without which it would be impossible to have a steady flame. Incidentally this causes more complete saturation with the gasoline vapor.

The support S consists of a loosely fitting piece of brass tubing, soldered to a brass plate, which is screwed down upon a block of wood. A couple of disks of thin sheet cork are placed at the bottom of the brass tube to lessen the danger of breaking the glass.

A Tirrill burner, intended for ordinary gas, is used. To prevent striking back it is capped with a loosely fitting piece of brass tubing, about one centimeter long, across one end of which a piece of brass gauze is fastened with hard solder. The gauze should not be coarser than 14-mesh, but if too fine some of the holes should be enlarged by forcing through them the sharpened tang of a file. A less satisfactory cap may be made by folding a piece of gauze over the end of the burner.

The compressed air is turned on full and the burner is so regulated as to give a non-luminous flame of the proper size. If the petroleum ether is too volatile, it may be mixed with gasoline. If the latter alone is used, the mixture soon becomes too poor and it is necessary to set the tube in a large beaker filled with moderately warm water. One filling of the tube furnishes gas for several hours.

After three or four years of almost constant use in this laboratory, the generator has proved entirely satisfactory and no accidents have occurred. The only precaution that may be mentioned, and even this is hardly necessary, is to extinguish the flame before turning off the supply of compressed air.

BUREAU OF STANDARDS
WASHINGTON

ADDRESSES

THE PATENT EXPERT AND THE CHEMICAL MANUFACTURER¹

By BERNHARD C. HESSE

By "Patent Expert" I do not mean that professional man who is called in by a litigant only at the critical or crucial stage

¹ Paper presented at the 48th Annual Meeting of the American Chemical Society, Rochester, September 8-12, 1913.

of a controversy long under way and most usually then in its final stages. On the contrary, I mean that professional man who is not only a highly trained and well equipped chemist, but who has also a natural or an acquired bent of mind which enables him to collect and assimilate the chemical and other facts relevant to the matter in issue, arrange them in logical

order, survey them critically and prepare them for submission to legal analysis and examination by patent counsel and who makes that particular occupation his vocation in life.

There can be no question that actual patent litigation between inventors or their principals is an unhealthy and an abnormal condition and is thoroughly disadvantageous to the commercial and industrial development of chemical inventions. The energy and ingenuity consumed in litigation could be applied much more profitably to the development of the enterprise itself than to a controversy over where the rights of the one begin and the rights of the other end.

It is perfectly safe to say that the great majority of inventors and their principals are anxious and willing to respect the rights of competitors. They are, however, hampered in the practical expression of this willingness by ambiguity, uncertainty and error in the statement of supposed rights as expressed in patents. It is to the elimination of these defects that the patent expert must chiefly address his efforts and thus ultimately justify and vindicate his activities and his position in this work-a-day world.

There can be no question that the most economical and profitable employment of a patent expert is at and during the development of a chemical invention itself—not after the patent has been issued and is in litigation. His chief and most useful function is to reduce the likelihood and cost of litigation to a minimum; this he can do only by a careful and patient examination and arrangement of all the relevant facts and by their proper submission to lawyers for final judgment, *before* the application is filed in the Patent Office.

This is merely a specific application of the old adage "An ounce of prevention is worth a pound of cure." While this may seem to many an obvious and self-evident course of procedure, yet only a minority of the chemical manufacturers and inventors in this country have regarded that course as being, in the long run, the advantageous and proper one for them to follow.

Any one who has actively participated in strenuous patent litigation and has had his share of responsibilities to sustain knows the feverish excitement and dissatisfying conditions due to hard work under extreme pressure, the extraordinary and unusual demands made upon the working staff of the litigants from the highest official down and the consequent unavoidable interference with the regular occupation and operation of staff and works in many, if not all, their divisions. He is also thoroughly convinced that any and all steps taken at the inception of the cause of trouble, namely, the invention and the patents based thereon to prevent such congestion and such high-pressure work must be, in the great majority of cases, far more profitable, economical and efficient than any attempt at correction or avoidance after the trouble has begun.

It would be idle to expect or to hope that all controversies as to the beginning and ending of rights could be eliminated by such careful preparation of a patent. That the points in issue would be reduced to a minimum is certain and it is equally certain that the meritorious issues in a case would not be smothered in a mass of minor, technical or irrelevant disputes, all, or at least the great majority of them, avoidable by care, caution and patience in the draft of the specification. The smaller the number of such minor points in a patent suit, the shorter the suit and the less expensive to the litigants while the Court and all others concerned are given an opportunity to concentrate attention and effort upon the points that really are meritorious and which alone should count.

It is safe to say that in the average chemical patent suit anywhere from 25 per cent to 50 per cent of the total litigation cost could have been avoided at the outset by proper, complete and non-ambiguous drafting of the specification and its claims and careful scrutiny thereof after allowance and prior to issue of the patent. A patent conservatively drawn, complete, clear and full in its disclosure as well as clear in its claims is far more

efficient as a protector against infringement of the invention involved and more certain of favorable adjudication than one not so drawn.

Chemical cases have been litigated in which a misplaced decimal point caused 8 per cent, a superfluous adverb consumed 12 per cent, an incorrect and superfluous theory used up 20 per cent of the total cost of litigation and finally, had a certain disclosure been just a little bit more explicit the litigation would not have been started at all. In still other cases had the relevant art been searched with an open and critical mind prior to patenting there never would have been any litigation. Further, the number of patents that have been rendered ineffective because of improper statement of invention, insufficient or incomplete disclosure is very great and most of these defects would or should have been avoided in the issued patent had there been suitable technical supervision and criticism such as by a patent expert. It is certainly easier and far less harrowing to examine and criticize an application even if it be your own work than to have to sustain an issued and faultily drawn patent when you have no chance for correction or alteration but must stand or fall by the document, "as is."

The pitfalls are many; there is no really dependable chart; each case must be treated on its own footing. The more careful the search, the more cautious the judgment and the fuller the knowledge of the relevant facts, the greater the fulness of disclosure, the more circumspect the phraseology and the greater the clarity of expression, the greater are the chances of success in avoiding useless points of attack, in minimizing effort and expense during litigation and the greater the protective value of the so-resulting patent to a meritorious invention. No amount of bolstering or shoring up *will* or *should* permanently help a non-meritorious invention.

THE PATENT CHEMIST—WHAT HE IS

The man whose business it is to attend to these matters I have referred to as a patent expert. This appellation is in itself something of a handicap to him in his work. There is no real reason why his expertness, real or assumed, in his special field should ordinarily be emphasized any more than in every-day life a skilled chemist is burdened with the designation of "expert." This man's real business is to be part and parcel of creative organization and machinery, not a man apart. Why not call him "patent chemist?" We have leather chemists, paper chemists, sugar chemists and the like. The patent chemist is one who specializes in the chemistry of patents, and patents in chemistry. Calling him "patent chemist" makes him on the surface at least more nearly part and parcel of the working staff than does the designation "patent expert;" the former name invites familiarity and coöperation, and suggests utility and work all of which is only helpful to those concerned, whereas there is a certain amount of aloofness or apartness, a suggestion of extraordinary and formal occasion and surroundings, of so-called "ornament," unconsciously, but none the less surely, associated with any term involving the word "expert."

THE PATENT CHEMIST—WHAT HE DOES

Now, this patent chemist, as I have called him, what does he do and how does he set about to accomplish it?

His usefulness begins with the inception of an invention and continues until the last bit of litigation is put out of the way, successfully or otherwise. He begins by getting a close understanding of the invention by careful, exhaustive and analytical study of the relevant prior art; he determines in his own way the presence of invention, defines the scope and nature of the invention, directs or requires confirmatory or exploratory work in determining and settling its scope; in other words, he formulates and "proves up" the statement of invention. Then he must see to a full and complete disclosure and finally a

proper wording, classification and subdivision of the claims. His next move is to take his tentative handwork to patent counsel to see how well or how poorly he has constructed his work; often working together they ascertain and locate weak spots and determine what shall be done to clear up, define and crystallize the situation.

THE PATENT CHEMIST, THE MANUFACTURER, THE INVENTOR AND THE LAWYER

So far, the patent chemist has acted largely as an avenue of communication between the inventor on the one hand who is a chemist and patent counsel on the other hand who is generally not a chemist. He must, in many cases, exercise great patience and ingenuity in getting the chemists' story into shape to lend itself to legal treatment, and on the other hand he must reduce the lawyer's story to such terms that the chemist understands and appreciates the situation.

More frequently than not, the patent chemist must hold the balance true as against the "fond-parent" enthusiasm, the disdain for real proofs and the airy generalizing tendencies of the inventor, the aggressiveness of the principal and the pessimism or cynicism of patent counsel, keeping his judgment calm, his reasoning sound and his facts straight throughout all this, not infrequently, very turbulent and trying period of patent-development.

The amount of labor, effort, study, investigation, reexamination, collecting of new facts or proofs and restating of positions and view points required of a patent chemist to reconcile these three elements is at times very great and difficult and always very trying, absorbing and engrossing.

To establish the usage of a certain expression in chemical publications may seem, at first blush, to be a perfectly simple matter but before the attempt to establish any particular usage has gone very far one is overwhelmed, more often than not, with a multiplicity of usages and choice becomes difficult if not impossible.

The question of what a publication, say, 40 years old meant in whole or in part to the man then writing it, to a man reading it 30 or 40 years later with all the intervening information at his disposal, is one whose correct answering may or may not interest the inventor or the principal, but patent counsel must know and the patent chemist must not only get that answer, but he must prove every part of it. The questions of analogy, homology and the like and their influence upon predication of invention are questions not always easy to answer, but whose answers patent counsel needs and the patent chemist again must supply and prove in their every part.

Practically all of the great variety of puzzling technical questions which conscientious, capable and competent patent counsel will propound in the course of developing a patent for a chemical invention resolve themselves into one or the other of the three above given and the road to the answer is not unusually long, hard and rocky.

Then comes the question of the accuracy, completeness, fullness, conciseness and clearness of one's own disclosure, the arguing back and forth over this expression and that expression, this or that sequence of ideas and so forth; the same is repeated on the statement of invention and finally it all has to be gone over again when the claims are taken up.

This kind of work is no occupation for a real chemist nor an inventor nor a principal. It is too slow for any of them; their entire mental attitude and habit of thought would have to be changed from an enthusiastic, creative state of mind based upon an abundance of relevant information to a cold, impersonal, analytic mental attitude based upon information, much of it not wholly relevant, but seemingly wholly foreign to the case; from the joyous and impetuous contemplation of his own creation the inventor would have to drop down to a very chill criticism of his own work as if it were the work of a total stranger. That

is for most inventors a practical impossibility, and it is only natural that it should be so.

Essentially the inventor in the usual course of his occupation must take chances—otherwise he would not be an inventor; essentially, those concerned in securing by patent what the inventor has achieved must take no chances and must be sure that no chances are being taken. It would certainly be extraordinary if both functions were to be successfully united in one and the same individual. Moreover, it as frequently as not takes more labor and effort to get a satisfactory specification together, than it takes to make and operate the invention. Very often, things on paper look very different from the real thing, but it is a most difficult operation to reduce those differences to comprehensible and concise written language. The average inventor would rather follow up the practical realization of his invention, or start something new and fresh than be obliged to go over and over the same old trail straining his eyes for something he does not care to see, and which does not hold nor grip his interest. His particular work is done; it is up to others now—the patent chemist and the patent counsel. They must dig into the relevant chemistry and the relevant court decisions, write and rewrite the specification and claims until, in their judgment, all foreseeable contingencies are provided for and taken care of.

THE PATENT CHEMIST AND THE PATENT OFFICE

At last, the specification is filed in the Patent Office and quite as often as not, the first Office Letter will show the patent chemist that he did not provide for all chemical contingencies and the patent lawyer that he did not provide for all law contingencies, or in the event they have done both they evidently did not succeed in saying so in a manner that *could not* and *would not* be misunderstood. Then the work must be taken up anew; explanatory letters must be written and many times these are not sufficient and personal interviews are needed to uncover the cause of the misunderstanding. Here again the patent chemist must take up the technical side of the case, which, as a rule, he can present conclusively far better than the patent lawyer just as the patent lawyer is far better able to present conclusively the law involved. Experience has shown, however, that law points are then far less frequently involved than are technical points.

If now the application, when in allowable shape, is put into interference it is the patent chemist who must in the last resort decide if the proposed interfering claims are, or are not such that his case can properly make; then the details of the interference proceeding and the preparation of the technical testimony direct and cross, for and against, should all pass the patent chemist's scrutiny. The quality and amount of work required of the patent chemist in such proceedings is dependent almost wholly upon the caution and alertness exercised by him during the development of the application.

When finally a patent is issued and negotiations for acquisition of rights thereunder are taken up it is the patent chemist who must expound the technical aspects of the subject to counsel for the other side and must again and again defend his work.

THE PATENT CHEMIST AND LITIGATION

However, the work of the patent chemist so far is a mere prologue to his work when a suit for infringement of patent is under way. Here is where he at times becomes actually the right hand of counsel and the real test of his ability and preparedness takes place. He must sift and test the evidence of infringement, he must scrutinize and forecast all possible and probable positions of his opponents, must have the entire mass of facts and data at his tongue's end; in fact, he must be a walking and living dictionary, guide book and cyclopaedia not only through the particular art and case involved, but into the most refined and subtle distinctions in any and every branch of chemistry which

even remotely touches the subject involved. The patent chemist frequently has the fate of the entire case entrusted to his keeping and his success depends not only upon how carefully he has prepared his case, but also upon the celerity with which he can produce his proofs and his alertness in anticipating or forecasting the moves, near or remote, of his opponents and preparing for them betimes. He must be able to do his work quickly and surely not only in the quiet of his laboratory or study, but more often under the strain of proceedings actually in progress and in the presence of his opponents. Not a single phase of the entire case must escape his attention and scrutiny. In one litigated case there was a total of 408 different chemical statements for each of which all the relevant facts had to be collated from the literature and the relevant testimony on both sides tabulated for use as the case progressed; the subject matter was relatively simple. What would have happened had that subject matter been really complex is wholly a matter of conjecture and fearful to contemplate. Other and more complicated cases have entailed quite as much if not more diffuse and wide-spread labor. Certainly no inventor wants to be pestered with such, for him, dry-as-dust details.

If the crucial test of a patent be its ability to withstand onslaught in the courts then the crucial test of the utility of a patent chemist is his ability to handle the vast amount of chemical facts involved with alertness, celerity and accuracy on such occasions. This will be rendered more certain and of a higher degree of efficiency the greater the familiarity of the patent chemist with the subject-matter and generally this familiarity is the greater, the longer the patent chemist has been associated with the subject. The same is true of the patent lawyer. Upon this assumption it further follows that the only wise policy is to commit the drafting of the specification and its prosecution in the Patent Office from the very start to that patent chemist and to that patent lawyer to whom the defense of the patent in the courts is to be finally entrusted. Let these men select the ground on which a dispute, if any, is to be conducted while they have an opportunity of so doing; let them shape the course and form of the document over which a struggle is expected and the results will be far more satisfactory than if those who are finally called upon to defend have no choice in the matter but must take things as they find them.

It is true that only a very small fraction of the issued patents is ever brought to the supreme test, and it would be a very wasteful policy indeed to expend upon patents of obviously little intrinsic value the same amount of labor that would be called for by a very valuable patent or set of patents. But as to a patent or patents of value there can be no two opinions as to the best general course to pursue, let those who must ultimately do the defending select their own ground while they may.

Many suits for infringement of patents are started or are proposed to be started, many more than actually find their way to trial in the Courts. In the preparation of the technical matter (both offensive and defensive) in such cases the patent chemist must clear up and maintain clarity in the technical questions involved because in such informal proceedings success demands completeness, celerity and alertness to almost the same extent and degree that the more formal court proceedings do. Many a contemplated litigation has not been started because of precisely such proper preparation of material prior to and during negotiations looking to amicable adjustment.

It is not only natural but inevitable that the state of known facts changes and shifts and becomes fuller as the inventive idea and the patent pass through the different stages just outlined and therefore judgment and opinion must frequently be tested and re-examined; these constitute the real cause for keeping the patent chemist in very close touch, in the majority of cases, with the growth and development of the invention as well as

with the business and all other similar conditions surrounding it.

THE PATENT CHEMIST AND THE CHEMICAL FACTORY

From this sketchy outline of the patent chemist, his field, his mode of operation and his relation to the manufacturer, it is no doubt clear that he is a man who must look at his chemistry not only with the eye and the mind of a chemist and of a manufacturer, but through the spectacles of a lawyer as well; he must look at patent law with the eyes of a chemist and the mental attitude of a lawyer and translate the law into chemical terms; he must know how to get convincing and correct answers to questions of great variety and scope, many of them seemingly trivial and simple, but at times of the utmost importance. He is neither a producer nor a creator of things; he is perhaps nothing more, in the final analysis, than a catalyst—a catalyst enabling two or more different agencies to operate in harmony and in complete understanding with each other and thus to increase the speed with which the object aimed at is achieved and with generally beneficial effect upon the quality of the final product. He may also be regarded as a foster-parent to the children of the brains of others and his function is to aid in their protection while in development. He is perhaps nothing more than an additional insurance against error in making plans for the future and his value grows with the value of those plans. He is not a lawyer, nor is he a real chemist, but he must be primarily and fundamentally a chemist with a chemist's instinct and a chemist's sympathies; he must have a working knowledge and an appreciation of all business conditions likely to influence the course of development of any and all of the inventions with which he is brought into contact; he is a mixture of chemist, manufacturer and lawyer and he must have an instinct and judgment for determining the correct time for, and the proper men to whom special questions must be submitted for final treatment. He must be especially alive to his own limitations and to those of others; he must not be unalterably wedded to his own opinions; he must be able, on occasion, to obliterate his own personality and to pocket his pride.

Now this brings me to the question of the status of the patent chemist in the organization or staff of a chemical factory. There can be no question that he must be in the confidence of the concern much more than the routine or works chemist; he must have greater freedom of action, greater radius of activity and his information should be first-hand wherever and whenever possible. He can make himself useful not only as above outlined, but also by keeping systematic track of what competitors at home and abroad are doing as foreshadowed in the technical press, patent applications and issued patents in all countries thus anticipating attempts to blanket or forestall his friends, but he may very often also be able to call to the attention of his principals new fields of endeavor and ways and means of entering them, which but for his watchfulness might escape notice. He should be made use of at every new manufacturing or operating step of his principals.

As to his position, should he be definitely inside or outside the organization, the answer is that it depends upon circumstances. In Europe, in some of the chemical branches, the patent chemists are fixed members of the organization, while in others the patent chemists are in business on their own account. Just how each or any organization shall handle that question involves the same questions as does the acquiring of any other commodity or service—by exclusive contract, by provisional contract or in the open market. Each concern must choose and decide for itself.

To put it in a very few words, the chief function of the patent chemist is to apply Davy Crockett's rule "Be sure you are right, then go ahead" to chemical inventions—a task not always interesting nor pleasant, but always useful and bubbling over with worth-while work

THE THEORY OF THE REMOVAL OF SUSPENDED MATTER FROM GASES

By W. W. STRONG

Received July 23, 1913

At the present time several processes are being used for removing suspended solid and liquid particles from gases, but no method has been indicated as to how the relative efficiencies of these methods can be compared. Indeed it is not well known what forces must be employed to secure the desired results. No accurate methods are in use whereby measurements can be made to indicate the amount of the suspended matter that has been removed from the gases. The purpose of the following paper is that of putting the whole subject upon a more exact and scientific basis.

"CLEARANCE" AND "PRECIPITATION"

In general, two methods are employed to express changes in the density of suspended matter in gases. If the suspended matter is of little value as is the case with coal smoke, copper fumes, etc., the density is usually measured by a photometric method. The Ringelmann scale is an example in point. The light employed is ordinary daylight. Probably the standard light for these purposes should be a light source possessing the same intensity curve as the sensibility curve of the average eye. The "clearance" of suspended matter by any process is the difference in the percentage of light transmitted by a unit volume of the smoke or fumes before and after the process was applied. Smoke of unit thickness absorbing 98 per cent of the white light of a parallel beam is subjected to washing. If it then absorbs 7 per cent of the light, the "clearance" would be 91.

Several difficulties are met in applying this method. The suspended matter may show a selective absorption of the light and thus color effects are introduced. The coefficient of absorption of light may not obey a law like that of Beers', *i. e.*, the absorption may not depend entirely upon the quantity of suspended matter in the beam of light but may also depend upon the density of the suspended matter. Each kind of suspended matter probably shows small variations of the above two types and these variations should be carefully considered.

The second standard method of measuring the amount of suspended matter in gases is that of filtering out the suspended matter from a known volume of the gas and weighing the filtered material. Unfortunately, there is no convenient and quick filtering apparatus of this kind available. (Probably the process of electrical precipitation is as practical as any and the writer is designing apparatus for this purpose.) This method is always used when the suspended matter is of value. The change in the amount of suspended matter per unit of volume due to any filtering or cleaning process will be called the "precipitation." Suppose the weight of zinc oxide per unit of volume of gas is 1.00. The dust is subjected to filtering by a bag and then contains a weight, 0.01 of zinc oxide per unit volume. The "precipitation" is then 99.

"DIFFERENTIAL" FORCES

In order to remove the particles of one substance from those of another with which they are intimately mixed, it is necessary to apply differential forces to the two sets of particles. In a gas the molecules are moving with very great velocities due to the heat motion of the gas. It is on account of this motion that gaseous substances diffuse among each other. Under ordinary experimental conditions, two gases will not separate from each other even though the masses of the molecules are quite different and the action of gravity is a differential one.

Nevertheless this separating effect of gravity does act even on the gases of the atmosphere. At great altitudes above the ground, hydrogen and the lighter gases preponderate. In the

lower strata of the atmosphere the percentage of the heavier gases is much greater. The greater the difference in the masses of the two particles and the smaller their velocity of heat motion the more rapidly will gravity cause them to separate. It is partly by this means that smoke and dust is removed from the air.

The separation (which gravity produces) of gases possessing different molecular weights has been discussed by Jeans, Einstein, Perrin and others. Fine dust, fume and smoke particles can be treated like large molecules from many points of view. In the case of particles suspended in liquids, Stokes' law is found to hold for particles as small as the larger hydrocarbon molecules.

The separation may be produced in other ways. The "centrifugal," like the gravity process, causes a separation of suspended particles from gases for the reason that the two sets of particles possess different masses. In washing, the effort is made to cause the suspended particles to unite with the washing fluid. (1) In these cases the separation is due to differential "mass" forces. Sieves of wire mesh, cloth, etc., are used. These sieves catch the particles of suspended matter on account of their larger volume. The gases have to be forced through the sieves by suctional or pressure forces. The separation here may be considered as being due to the action of (2) differential "volume" forces.

It is well known that there is a region near a heated surface from which dust particles are driven. This action is somewhat similar to the pressure on radiometric planes (Crookes' radiometer) taking place at low pressures. The dust particles are subjected to a greater molecular bombardment in the direction of the heated surface and are therefore forced to move in the opposite direction. Light and heat cause a pressure somewhat similar in nature and this accounts for the repulsion of comets' tails by the sun. The "pressure" may be due to the heat motion of molecules, the radiation pressure of heat, light and electromagnetic waves or to streams of ions. This separation of particles from a medium will be considered as being due to (3) differential "radiation" forces.

The suspended particles may be subjected to the action of an electric or a magnetic field. If the particles are magnetic they will be set into motion. As few kinds of dust particles are magnetic and as this action is similar in kind to that of the electric field, it will be included under the latter action. The action of the electric field is of two kinds. The field may not be uniform. The particles may possess a different dielectric power from that of the medium and will therefore be caused to move by the non-uniformity of the electric field. In other words, the particles become polarized. Water drops can be separated from oil and gold may be separated from quartz in this manner. The separating force in this case will be called (4) the differential "force of polarization."

The suspended particles may be charged by causing them to unite with ions. If they are then subjected to the action of an electric field they are immediately set into motion with reference to the surrounding neutral particles. The method of electrical precipitation is based upon the use of streams of ions to charge the suspended particles and the above action of the electric field to remove the charged particles from the gas. The separating force here is (5) a differential "ionic" force.

THE COMPARATIVE EFFICIENCY OF THE DIFFERENTIAL FORCES

The law describing the way particles can be removed from a gas has been given by Stokes and has later been modified by Cunningham and others. The statement of the law will be given in the section on "settling due to gravity" because the verification of the law by various investigators has been made by the use of gravitational forces. Centrifugal and electrical forces will act in the same manner.

The basic law underlying the phenomena of the separation of suspended particles from fluids is of the Stokes' type, the

constants of which will be a function of the density, shape, size and nature of the surface of the particles, and the pressure, viscosity, temperature, density and nature of the fluid. Assume that the particles are smoke particles, and that the fluid is a composition of air and carbon dioxide. The force that must be applied to separate a particle from the gas depends upon the Stokes law that holds for these conditions, the distance the particle must be moved and the time that is to be allowed for this movement to take place.

The efficiency of the process of removing particles from fluids can be defined in several ways. Let us assume that the efficiency of the given process is unity when the particle is caused to move with a velocity of a centimeter per second. The work done on the particle under these conditions will be represented by the force term given by a law similar to that of Stokes, since the distance over which the force has caused motion is in this case unity. If the time were made very long the applied force could be made very small. If it is required that the velocity should be greater than that given by the definition, a greater velocity may be used and the comparison of the efficiency of different precipitating agents based on this velocity.

The efficiency of any process used for removing particles from fluids will be the ratio of the energy required to cause the separation of the particles determined by a law such as that of Stokes and the amount of energy used by the given process.

Let us take a concrete example. A certain kind of smoke contains 1,000,000 particles per cu. cm., the smallest particles having a diameter of 0.0001 mm. Let us assume that the particles are all of the same size, the size of the smallest particles. Let us also assume that the separation of the particles from the gas can be made complete if the velocity of the particles is made a centimeter per second relative to the gas itself. Let it be necessary to move the particles 2 cm.; let the force required by Stokes' law to give a velocity of 1 cm. per second be F ; let X cu. cm. of the smoke be treated per sec. The amount of work done per second is: $1,000,000 X 2 F = S$ per sec.

If the smoke is passed through a centrifuge, the differential force acting upon the smoke particles will be the centrifugal force and this should be equal to F . The energy used per second (C) to run a centrifuge that cleans X cu. ft. of smoke per second will be very largely lost in friction and windage. The efficiency of this process will be S/C .

In the method of electrical precipitation a certain wattage loss of energy (W) will represent the electrical discharges in the smoke. Some of this energy will be spent in effecting chemical reactions and in heating the gases. The efficiency of this method is S/W . A method of treatment like the above will indicate the ultimate theoretical possibilities of these various methods.

From an engineering point of view the problem is much more complicated. If large chambers are available and the volume of smoke or fumes is comparatively small, settling by gravity will probably be the best method available. If the smoke gases are cool and a large draft is available, filtering could be made quite efficient, especially if the smoke particles are large in size. Centrifugal methods can readily be used if the suspended particles are of large size. The short treatment following is theoretical. One reason for this method of treatment lies in the fact that our engineering knowledge along these lines is very incomplete and unreliable. In many cases no definite information is given of the character of the smoke or fumes to be treated.

THE DIFFERENTIAL "MASS" FORCE

One of the most important of the problems in mechanics is that related to friction or viscosity. We all know that a feather and stone fall with the same velocity in a vacuum. Why do they not do so in air? The answer is—a feather meets with resistance or friction in its course through the air. The frictional resistance due to the settling of smoke and dust particles in the atmosphere is therefore the same as the resistance which an aero-

plane meets in flying: the resistance which causes shooting stars to burn and heats meteors and which causes mists and fogs to remain suspended. It is for this reason that small raindrops fall very slowly, while large drops, such as are formed during thunderstorms, fall very rapidly.

In the case of falling raindrops there is in general an equilibrium between the forces of friction and the pull downwards by gravity. The more slowly a particle falls the less resistance does it experience. A raindrop will therefore continue to be accelerated until the frictional forces which it experiences just balances the attraction of gravity.

In the upper strata of the atmosphere where the air density is very small, dust particles would fall very rapidly. In the outer portions of the solar corona dust particles would probably gravitate rapidly towards the sun, due to two causes, the great attraction exerted by the sun and the rarity of the atmosphere. In certain cases, however, the high temperature and the pressure of radiation will act so as to cause certain particles (whose size and density lie between certain ranges) to remain suspended. This pressure on the particles is exerted by the light and heat radiations striking the dust or smoke particles. If the beams of radiation are more intense in one direction (this is often the condition in certain parts of a furnace) the dust particles will be acted upon by a force in the same direction as that of the radiation. The effect of high temperature is to increase the viscosity forces.

In a very interesting paper (*Math. and Phys. Papers, Cambridge, 3, 55*), G. Stokes has discussed the effect of viscosity on the movement of a pendulum. Incidentally he took up the motion of a sphere (radius a) moving with a velocity, V , in a medium having a viscosity of $\mu\delta$. If X is the resistance to the motion of the sphere and Δ is its density and δ that of the medium, then $X = 6\pi\mu aV\delta$.

For a sphere falling under the action of gravity

$$6\pi a\gamma V = 4/3\pi a^3(\Delta - \delta)g.$$

The fall of raindrops that have reached a maximum and final velocity, the settling of fumes, dust and smoke in gases, even though the particles are not perfectly spherical, follow a law such as that of Stokes. These conditions require the fluid or gas through which the particle falls to be in a state of rest.

Perrin has shown that the law of Stokes applies to particles of ultramicroscopic size even though the particles undergo the Brownian movement.

Rybczynski and later Hadamard have (*C. R., May, 1911*) developed a slightly different formula for a sphere of density Δ_1 and viscosity γ falling in a medium of density Δ and viscosity γ_1 .

$$(\Delta_1 - \Delta)g = 2/9 \gamma V [a^2 \gamma_1 + 2/3 \gamma_1 \gamma + \gamma]$$

Applying this formula to water drops [$\gamma = 1057(10)^{-8}$] falling in air [$\gamma_1 = 18(10)^{-8}$] one finds that the velocity given by the law of Stokes should be multiplied by the factor 1.006.

In order to apply the above formulae to the settling of fumes or smoke in chambers it is necessary to know the size and density of the particles to be considered, the viscosity of the medium and the distance it is necessary for the particles to fall.

In general, gravity is not great enough to cause particles to move with sufficient velocity, especially if the particles are very small. Under these conditions particles may be caused to unite with liquid sprays or become nuclei for the condensation of vapor. This causes an increase in mass. Sound, electromagnetic radiations and an electric field may also be employed to cause an aggregation of the particles. Large differential "mass" forces may be obtained by centrifugal processes.

If a particle of mass m is caused to rotate about an axis with an angular velocity w , the distance of the particle from the axis being r , then the force that must be exerted upon the particle to keep it moving in a circular path of radius r is mrw^2 .

In a centrifuge the gaseous medium should possess an angular velocity of ω . The two forces that will operate on the particle when its distance r from the axis increases will be that of frictional viscosity and the centrifugal force

The centrifuge process is frequently used when the particles to be separated from a gas possess considerable mass. Under these conditions ω need not be so great. It is very doubtful if a process of this kind would be practical in the case of small smoke particles. A combination of a washing (or an electrical discharge) and a centrifugal method might be found to be better than any single method used by itself.

The efficiency of the "volume" forces depends upon the pressure required to force the gas through the sieves. The nature of the differential "radiations" have been worked out mathematically but these have no value as a practical method of removing suspended matter from gases. Neither is polarization a practical method. Probably one of the most important from the efficiency point of view is the differential ionic force.

THE DIFFERENTIAL "IONIC" FORCE

The use of electromagnetic fields for removing suspended matter from gases and liquids is practically limited to the action of the electric field. This condition is due to the fact that very few suspended particles possess any appreciable magnetism. Even nickel dust would be removed with difficulty by the action of a magnetic field. This leaves only iron and a few magnetic compounds of iron that can be acted upon by a magnetic field.

In general it may be said that the application of electric fields is restricted to a non-conducting medium, such as a gas or a dielectric liquid. There are no gases that conduct naturally. The ions or carriers in a gas must be produced artificially. Conducting liquids are electrolytes and these contain spontaneously generated ions. These liquids support only a small difference of potential and conduct by electrolysis. When electrolysis takes place gas usually accumulates at the electrodes, thus causing an added resistance to the flow of current.

The separation of suspended solid and liquid particles from a non-conducting gas or liquid is therefore dependent upon the action of electric fields possessing an intensity ranging between several hundred to several thousands of volts per centimeter. This action of an electric field is not as simple, however, as it might appear to be. The suspended particles may be caused to combine with each other (aggregation); they may be in a state of polarization and they may become charged.

In the case of suspended matter in gases the important item is that of charging the particles. The efficiency of the process depends upon the thoroughness of this charging process.

Like the other processes used for cleaning gases, the electrical process causes an expenditure of energy that is proportional to the volume of gas rather than proportional to the amount of matter suspended in the gas. No one has devised any cleaning process of the latter type although certain automatic devices promise to make the electrical process active only when there is a certain density of the suspended matter.

The writer¹ has determined the energy loss in the electrical precipitation method to be about 400 watts for treating gas at the rate of 1000 cubic feet per minute. This energy loss does not vary greatly between 0° and 200° C.; does not vary with the velocity of the gas, with the density of the suspended matter or with the composition of the gas. In order to compare this efficiency with the "perfect" efficiency given by Stokes' law it would be necessary to determine the number of particles and the average amount of energy required to remove each particle from the gas by using Stokes' formula.

A very rough calculation of the efficiency of the electrical method may be made by assuming Broghé's data for cigarette smoke. The radii of these smoke particles range between 0.1 to 0.001 μ and in each cubic centimeter there are several

million particles. Assume that the particles are to be given a velocity of 20 centimeters per second and that the average radius is 0.00001 centimeter:

$$F = 6\pi(0.00001)(\mu = 0.000178)(V = 20)$$

Let the particles be moved a distance of 8 centimeters and suppose there are 30,000,000 particles per cubic centimeter. Since 1000 cubic feet contain 2.8317(10)⁷ cubic centimeters, the required work in watts will be:

$$W = 8F \times 30,000,000 \times 2.8(10)^7 = \text{about 40 watts}$$

This would indicate that possibly 15 per cent of the electrical energy may be expended in cleaning the gas, this energy being converted again into heat energy through the agency of the viscosity forces.

In the above calculation it must be recognized that the data are extremely meager. It is to be hoped that theoretical investigators will take up a detailed study of these problems.

DEPARTMENT OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH

THE UTILIZATION OF SEWAGE¹

By GEORGE A. SOPER²

It is often supposed that the discharge of sewage into rivers and harbors represents a great economic waste and many persons, among them some eminent scientists, have, in times past, proposed that cities should conserve the manurial value of their sewage. Victor Hugo was an ardent advocate of this form of conservation and Liebig, Hoffman and Crookes have raised their voices in solemn warning against the waste. Such warnings are well remembered and the question is frequently asked—Why should the sewage of our cities be discharged without any attempt being made to utilize it and return the useful ingredients to the soil?

To answer that it costs more to utilize the manurial ingredients than they are worth does not answer the question with sufficient fullness.

The principal reason why it is impracticable to utilize the manurial ingredients of sewage lies in the extremely diluted state in which the useful ingredients exist. There are few processes known to the technical arts by which such immense volumes of liquid can be successfully treated for the extraction of their valuable materials. Sewage is over fifteen times as dilute as sea water and the ammonia, phosphoric acid and nitrate in sewage are, like the gold in sea water, there unquestionably, but mingled with so much that is useless that they cannot be extracted without too great expense.

Sewage may be considered to consist of two parts of solid matter in 1,000 parts of water; and of this solid matter only a portion has any value in agriculture. Contrary to popular opinion, sewage contains relatively little excrement either liquid or solid, the explanation of this fact lying in the large amount of water used in flushing the closets and for the many objects not connected with the disposal of excrement for which the water is used. The per capita consumption of drinking water in a modern American city ranges from about 75 to over 200 gallons per 24 hours.

The City of New York and the other municipalities in the metropolitan district contained, in the year 1910, 6,019,000 inhabitants and produced over 765,000,000 gallons of sewage per 24 hours. This sewage contained over 658 tons of suspended matters, of which about one-half was nitrogenous. It has been estimated that the excrements of a mixed municipal population should be worth, on theoretical grounds, from \$1.00 to \$1.25 per capita per annum, from which it appears that the metropolitan district is throwing away between \$6,000,000 and \$7,500,000 every year.

¹ Paper presented at the 48th meeting of the American Chemical Society, Rochester, September 8-12, 1913.

² President, Metropolitan Sewerage Commission of New York.

¹ Trans. A. I. E. E., June, 1913.

To utilize this sewage, it would be economical to build works whose running expenses, interest charges and allowance for depreciation and repairs would not exceed, say, \$6,000,000. There would be clear gain in transforming the present polluted harbor into a clean and wholesome natural body of water, although this gain would not be measurable in terms of currency. Allowing 10 per cent to cover all charges, it should be good business to borrow \$60,000,000, if, by so doing, works could be constructed and operated so that the value of the sewage would be completely utilized.

Sixty million dollars would not be nearly enough. In addition to the treatment works themselves, large sewers would have to be built to take the sewage to the works and carry the purified effluent away. Pumps would be necessary in order to move the sewage through the conduits. Land would have to be purchased upon which to build the plant. A large corps of employees would be required for the management and conduct of the process and for the sale of the product. Over all there would have to be a strict, sanitary supervision wielding the autocratic power which rightly belongs to public health officials in matters where life and comfort are balanced on one side against shrewd commercial enterprise on the other. And it may not be amiss to state here that desire of profit in the disposal of sewage has repeatedly been found in the past to be strongly opposed to the interests of sanitation.

It may be well to consider for a moment what has been accomplished toward the utilization of sewage. Briefly, such works are of two classes: *First*, those which provide for the direct application of untreated sewage to land; *Second*, those which provide for the extraction of the utilizable ingredients by means of suitable mechanical devices.

The application of the sewage to the soil was for many years persistently attempted in England and there are now in that country and in other lands sewage farms which afford excellent opportunities to study what it is practicable to do in this direction. The testimony of agriculturalists and economists is all of one sort. Sewage farming does not afford a satisfactory method of utilizing the useful ingredients of sewage, except under unusual circumstances, as, for example, where the contained water is needed for the crops.

With respect to the extraction of the useful ingredients nothing favorable can be said. There are no works in the world which deal with sewage of average quality from which all or nearly all the theoretically useful ingredients are extracted without costing more money than they are worth. Efforts have been made in abundance to devise plans by which commercial fertilizers could be produced; scores of patents have been taken out and many companies formed to make a business of extracting the useful materials, but these ventures have proved disastrous.

The search for a profitable method of extracting the useful ingredients of sewage is rendered especially difficult by reason of the physical and chemical condition of the sewage. Coarse materials, if floating, can readily be removed by screens and, if heavy, they will promptly subside in settling basins. But a large part

of the materials characteristic of sewage is in the colloid state and can neither be screened nor settled, except with much difficulty. The best settling that has been done produces sludge which contains over 95 per cent of water and persistently resists attempts at further concentration.

The sludge problem is recognized to be of central difficulty in sewage disposal, for the sludge cannot be applied to land with profit nor can its utilizable ingredients be extracted without more cost than they are worth. The sludge therefore causes embarrassment scarcely second to that produced by the sewage from which it is obtained. Apparently, there are but few things that can be done with sludge even if the sole object is to get rid of it without nuisance. It can be fermented with the production of large volumes of methane and other gases of small value and a humus-like residue from which the liquid readily drains off.

This sludge, when drained and dried, can be burnt. Sludge can be dug into the ground and, if not applied in too large quantity, in course of time it will disappear. The most usual method of dealing with sewage sludge is to transport it by pumping, cartage or tank steamer to some remote point where it can be dumped, simply with the object of getting rid of it.

The outlook for the future need not be discouraging because of the failures of the past. There may yet be found some method for the production of dense sludge and the extraction of its utilizable ingredients. If the physical state of the colloid particles could be altered so that they would part with the large amount of water which they contain, these particles should settle rapidly and dense sludge be produced. If the sludge could be further concentrated either by centrifugal action or otherwise, considerable advantages would be gained.

An inviting field lies open for the inventor of a successful process for the utilization of sewage, for there are hundreds of cities, and among them the largest in the world, which will give the raw material without imposing any other obligation than that reasonable sanitary requirements shall be observed. The City of London has for years advertised that its sewage was ready for anyone who wanted it, but the nearest approach to an acceptance of this offer was from a company which, after many promising arrangements, went out of business without taking a gallon of sewage away.

A process for the utilization of sewage may be of value even if it does not recover sufficient of the useful ingredients to completely meet the cost of obtaining them. If the cost of treating the sewage can be reduced by half or even less, the economic return may be sufficient to warrant a wide employment of the scheme, it being remembered that the prime object in installing sewage disposal plants is to get rid of the sewage without offense.

The recent contributions of science to the art of sewage disposal have been directed almost exclusively to the disposal of the wastes in such a way as to be permanent and sanitary and as inexpensive as possible. In nearly all works constructed within the last few years, the point of view has been that sewage was a thing to be gotten rid of and in getting rid of it there was no prospect of any useful return.

17 BATTERY PLACE, NEW YORK

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

THE STATUS OF THE CEMENT INDUSTRY

The total production of the cement mills in the United States in June, 1913, was 2 per cent less than in June, 1912, and on July 1, of this year, less than 60 per cent of the cement kilns in the country were in operation; this was attributed to the prevailing hesitancy in the undertaking of constructive enterprises on a large scale. However, owing to the accumulation of orders

received at an earlier period, the June shipments continued large, approximating 8,000,000 barrels—about 1,000,000 barrels in excess of the actual output. The surplus stocks at the mills on July 1 totaled 10,000,000 barrels, an increase of 6 per cent over last year.

According to *The Journal of Commerce*, the significance of the cut in production may be better realized from the fact that for

LEHIGH DISTRICT CEMENT PLANTS

NO	NAME	LOCATION	RAILROAD	Capacity in bbls. per day
1	Northampton Portland Cement Co.	Stockerton, Pa.	Lehigh & New England	1,800
2	Nazareth Cement Co.	Nazareth, Pa.	Lehigh & New England	3,300
3	Phoenix Cement Co.	Nazareth, Pa.	Lehigh & New England	1,000
4	Dexter Portland Cement Co.	Nazareth, Pa.	Lehigh & New England	2,400
5	Penn. Allen Portland Cement Co.	Nazareth, Pa.	Lehigh & New England	2,000
6	Pennsylvania Cement Co.	Bath, Pa.	Lehigh & New England	3,000
7	Bath Portland Cement Co.	Bath, Pa.	Lehigh & New England	3,000
8	Lawrence Cement Co. of Pennsylvania	Siegfried, Pa.	Central of New Jersey	3,500
9	Atlas Portland Cement Co.	Northampton, Pa.	Central of New Jersey	46,000
10	Whitehall Portland Cement Co.	Cementon, Pa.	Lehigh Valley	1,250,000
11	Atlas Portland Cement Co.	Coplay, Pa.	Lehigh Valley	46,600
12	Lehigh Portland Cement Co.	West Coplay, Pa.	Lehigh Valley	36,600
13	Coplay Cement Manufacturing Co.	Coplay, Pa.	Lehigh Valley	5,000
14	American Cement Co. of New Jersey	Egypt, Pa.	Lehigh Valley	6,500
15	American Cement Co. of New Jersey	Lesley, Pa.	Lehigh Valley	6,500
16	Lehigh Portland Cement Co.	Ormdorf, Pa.	Lehigh Valley	36,600
17	Lehigh Portland Cement Co.	Fogelsville, Pa.	Phila. & Reading	36,600
18	Edison Portland Cement Co.	New Village, N. J.	D., L. & W.	8,000
19	Vulcanite Portland Cement Co.	Vulcanite, N. J.	Central of New Jersey	5,500
20	Alpha Portland Cement Co.	Alpha, N. J.	Lehigh Valley	18,000
21	Alpha Portland Cement Co.	Martin's Creek, Pa.	Pennsylvania	18,000

the first six months of the year the production of 39,000,000 barrels was nearly 25 per cent ahead of last year, while shipments were 14 per cent larger than for the first half of 1912. Surplus stocks increased nearly 3,000,000 barrels in the half year.

The Lehigh district, a map of which is presented herewith, seems to be following the trend of orders more closely than a few years ago, when market conditions were quite chaotic; this district supplies about one-third of the American cement pro-



duction. The Lehigh production fell 10 per cent in June, while shipments increased 3 per cent as compared with those of June, 1912. Seventy-five per cent of the Lehigh kilns were active on July 1, 1913, but the surplus stocks at the mills on that date, amounting to 3,000,000 barrels, were only 4 per cent larger than last year. Producers in the Lehigh district have taken steps to prevent market demoralization by reducing their output; as a result of this policy, prices are being fairly well maintained.

THE BECKTON GAS LIGHT AND COKE COMPANY OF LONDON, ENGLAND

The Beckton Gas Light and Coke Company, which supplies gas for two-thirds of the British metropolis, is described in the *American Gas Light Journal*, 99, 34.

At the river pier some 1,750,000 tons of coal are unloaded per annum, the hydraulically operated grabs being capable of handling 700 tons per day. The retort houses are 14 in number, and extend about half a mile, in double line. Some are electrically operated, others have the aid of compressed air, and a third variety is provided with hydraulic machinery. Jointly the retorts are capable of producing 61,000,000 cubic feet of gas per day, and of carbonizing 5,000 tons of coal. In addition, there is a carbureted water-gas plant capable of producing 27,000,000 cubic feet of gas per day. The plant is stated to be the most complete in existence, all the operations of gas-making and recuperation being controlled by hydraulic power operated

by levers from a central stand. The blowing plant for this installation consists of four 110-horse power turbine-driven fans. The carbureted water gas, after being tested, is mixed with the coal gas at the inlet of the gasholders, of which the storage capacity totals 19,000,000 cubic feet, the largest gasholders holding 8,000,000 cubic feet.

A pumping plant capable of pumping 4,100,000 cubic feet of gas per hour delivers the gas to the storage holders or for use in London. There are extensive repair workshops, including the boiler shop for the repair of all stationary and locomotive boilers, and other work of a similar nature. There is a foundry capable of producing some 50 tons per week, with a pattern-making shop in connection therewith. The private locomotive sheds of the works provide accommodation for 31 locomotives, and these are engaged upon 45 miles of single track.

In the tar works are stills for the distillation of 18 million gallons of tar per annum, with underground storage for 4,000,000 gallons. The five pitch beds adjoining the stills have a capacity of 30,000 tons. For the refining of the light oils the naphtha stills and washing plant prepare the distillate which, in the benzol house, yields benzol, toluol, and solvent naphtha amounting to 120,000 gallons yearly. Naphthalene is refined by means of 12 stills, and is manufactured into salable forms in a house close by. Another battery of stills serves for the purification of carbolic acid, up to the standard required for surgical purposes. A series of large tanks contains the stores of creosote used for timber preserving, very large quantities being produced. In another quarter is the house in which anthracene is purified.

The liquor works contains stills and saturators producing 24,000 tons of sulfate of ammonia per annum. Beside it stand a sulfuric acid plant in which sulfuric acid is manufactured from the spent oxide resulting from gas purification; the furnaces are of modern mechanical type. Ammonia gas is also purified for the manufacture of aqueous ammonia and for the production on a large scale of anhydrous ammonia (for refrigerating plant). In the cyanogen plant crude cyanogen liquor is converted into crystalline prussiates of soda and potash, and provides material for the manufacture of Prussian blue and for the cyanides of potassium and sodium.

THE MODERN BY-PRODUCT COKE OVEN

In the *Monthly Bulletin of the American Iron and Steel Institute*, 1, No. 5, are published several papers relating to the present status of the by-product coke oven in the United States.

Meissner expressed the opinion that when located at points suitable to its requirements, the by-product coke oven was the most satisfactory and economical yet known for the manufacture of metallurgical coke. In the last six months of 1912 coke

was produced at the rate of 2,900,000 tons per year at the Gary, Ind. by-product coke oven plant, on a mixture of 76.4 per cent Pocahontas and 23.6 per cent high volatile coals. The conservation of coal through producing this amount of coke in by-product ovens instead of bee-hive ovens amounts to about 1,190,000 tons per year. It has been found by the United States Steel Corporation that the coke produced in by-product ovens, when properly made, is fully equal in quality to that obtained in bee-hive ovens; and that it is possible to utilize a larger variety of coals, when properly selected and mixed, including coals which up to the present time have been practically regarded as "non-coking," and make a highly satisfactory metallurgical coke. The by-product plant can be erected near the blast furnaces and it is practicable to ship to it coking coals from any radius within favorable freight rate; this, however, is not the case with the bee-hive ovens, which, in most cases, are placed near the coal mine which supplies the coal, and, when the mine is exhausted, the bee-hive plant has to be abandoned.

Blauvelt pointed out that the first ovens in this country coked 4.4 tons of coal per oven per 24 hours, and that 25 ovens, with a carbonizing capacity of 110 tons a day, were regarded as the proper unit for one crew of men. "The oven of to-day is carbonizing 20 tons per day, and practically the same crew of men, with the help of modern machinery, will handle 50 ovens or more, carbonizing 1,000 tons per day." He stated that from 40,000,000 to 50,000,000 feet per day of illuminating gas from coke ovens are now produced and sold in the United States. The following points were indicated by Blauvelt as important to a well-designed oven: Largest yield of surplus gas; ability to substitute producer gas for oven fuel gas; maximum yield of by-products; maximum yield of good coke; shortest coking time; lowest cost of operation and repairs; simple and strong, with weight properly distributed.

Atwater called attention to the fact that the recovery oven has achieved a definite place as a part of the steel-making process, and that it presents economies and advantages with which the present-day steel manufacturers must reckon. Meissner had referred to the employment of benzol as a motor fuel; Atwater cited the case of a truck engaged in general city delivery work. On a six months' test with benzol alone as a fuel, a gallon of benzol yielded 15 per cent more work than a gallon of gasoline; based on an equal number of heat units supplied the efficiency was about the same.

"NERADOL D", A SYNTHETIC TANNIN

Stiasny, in the course of a paper on artificial tannins,¹ gives an account of the production of "syntans" (synthetic tannins), one of which products has been placed on the market by the Badische Company, Ltd., under the name of "Neradol D." Syntans are condensation products which may be produced either by heating phenols with formaldehyde in a slightly acid solution and solubilizing the resinous products thus obtained by means of sulfuric acid, or they can be made by first sulfonating the phenols and then condensing them with formaldehyde under such conditions that only soluble products are formed.

"Neradol D" resembles, in its appearance, a vegetable tannin extract of bright color. The analogy between this product and natural tannins is shown by the following behavior of "Neradol D": Its water solution is of a semi-colloidal character, passing a semi-permeable membrane only slowly and giving a precipitate with gelatine solution. Iron salts produce a deep bluish violet coloration, and a 10 per cent solution of iron alum is a suitable means of controlling the course of "Neradol D" tannage; this is done by placing a few drops of the iron solution on the fresh cut of a half-tanned hide, when the tanned layers are colored deep blue. Lead acetate as well as aniline hydrochloride give precipitates with "Neradol D." Stiasny makes

special mention of the very bright color of solutions of "Neradol D" and of the complete solubility in cold water—distinct advantages over the ordinary tannin extracts.

It is said that the real character of "Neradol D" is that of a light leather tannin, and that sumach and gambier are those natural tannins whose effects have the greatest resemblance to that of "Neradol D." It may be used as a bleaching agent of dark-colored leather; in this case the retanning action of this artificial tannin prevents loss of weight, which accompanies most of the usual methods of bleaching heavy leathers.

THE CAUSES AND PREVENTION OF SEWER PIPE FAILURES

It has been stated that, with the inclusion of cement pipe and the cost of labor and materials, it is probable that \$75,000,000 are spent annually in this country in the construction of sewers and drains. This expenditure has been largely based upon a visual examination of the pipe or tile, and a conjectural inference as to the loads which it may be expected to carry safely. With a view of developing a correct method of calculating the loads on pipe and of preparing adequate standard specifications for the quality of drain tile and sewer pipe, the Engineering Experiment Station of Iowa State College has conducted a series of experiments, the results of which are reported by *Engineering Record*, 68, 46; these are presented at some length on account of their interest to the ceramic and sanitary engineer.

The following general conclusions reached as to the failure of drain tile and sewer pipe in ditches are based on extensive data obtained from drainage engineers:

1. There have been a large number of failures of drain tile and sewer pipe by cracking in ditches, and there is a wide prevalence of cracked pipe in existing sewers and drains. The cracking is generally confined to pipe larger than 14 in. in diameter. Engineers have not properly appreciated either the extent or the importance, nor have they fully understood the causes, of cracking of drain tile and sewer pipe in ditches.
2. The principal cause of the cracking of the drain tile and sewer pipe in ditches is simply that, as at present manufactured, sizes larger than 15 in. in diameter are very generally too weak to carry the weight resting upon them from more than a few feet depth of ditch filling.
3. In very many cases it is entirely impossible to prevent cracking in ditches of drain tile and sewer pipe as at present manufactured by any possible reasonable amount of care in bedding and laying the pipe and refilling the ditches. A material difference in the carrying power of the pipe, however, can be made by proper care in bedding and laying.
4. Drain tile and sewer pipe crack more readily in ditches with hard bottoms than when laid on slightly yielding soils.
5. It is reasonable, advantageous and necessary to require the pipe-laying contractor carefully to shape the bottom of the ditch to fit the under half of the pipe surface, and to bed the pipe carefully for this distance in sand or granular soil, so as to secure a firm, uniform bearing.
6. Drain tile and sewer pipe are so rigid and crack from such slight distortions, as compared with the yielding of the most solidly tamped earth filling, that it is not feasible to prevent cracking by tamping the ditch filling on each side of the pipe at the midheight. Such side tamping, however, should always be required, and thoroughly done, for it is of great value in preventing the collapse of pipe after it is cracked.
7. Where the pipe is found to crack in spite of faithful observance of the specifications stated in 5 and 6 above, the only effective remedy, other than using stronger pipe, is to bed the pipe in concrete up to the midheight. Such concrete can be lean, and need not be thick if the soil is firm, but must thoroughly fill all spaces between the lower half of the pipe and the bottom and sides of the ditch.

¹ *Chem. World*, 2, No. 7, 216. See also *THIS JOURNAL*, 5, 705

8. The width of the ditch at the level of the pipe makes a great difference in the weight of filling resting on the pipe, this weight being greater the wider the ditch. Moreover, the narrower the ditch at the midheight of the pipe, the more effective is the side support against the collapsing of cracked pipe.

9. Where the ditch filling over the pipe is rammed in layers during refilling, there is serious danger of cracking large drain tile and sewer pipe [by using too heavy rammers and too thin a layer just above the pipe].

10. While large amounts of cracked drain tile and sewer pipe are standing without collapsing in existing drains and sewers, the stability of cracked pipe must be considered precarious, as has been demonstrated by numerous collapses.

11. Cracked pipe is especially dangerous in tile drains and storm sewers, for the reason that, in the best engineering practice, it is not found practicable to make the capacity of drains and sewers equal to the most exceptional floods. Hence they are certain eventually to be overcharged, and to run under pressure, and the collapse of cracked pipe is likely to result at such times from the softening of the soil by water escaping through the joints and cracks.

The general principles of the theory of loads on pipes in ditches, which were borne out by a long series of laboratory and field tests, may be in part summarized as follows:

1. The weight of the filling in a drainage or sewerage ditch, at the time of maximum load on the pipe, is carried partly by the pipe, and partly by friction against the sides of the ditch. Cohesion greatly reduces the loads carried by the pipe at ordinary times, after the ditch is refilled and partly consolidated, except in the case of clean sand, or gravel filling, but does not appreciably affect the maximum loads.

2. The maximum loads on pipes in ditches, due to the weight of ditch-filling materials, will usually occur at the time of the first very thorough surface flooding of the ditch filling after construction, when there is a large settlement of the refill, but there is possibility of their occurring later, at the time of extreme saturation of the ditch filling by surface flooding of the ditch and by overcharging of the drain or sewer. The maximum loads may even be postponed for many years in some cases, as is frequently shown by settlement of the filling in old ditches during paving construction.

3. Safe values of the ordinary maximum loads on pipes in ditches, due to the weight of ditch-filling materials, can be computed by the formula $W = CwB^2$, using the values of C given where W = load on pipe in ditches, in pounds per linear foot; C = coefficient of loads on pipes in ditches; w = weight of ditch filling material, from 50 to 120 lb. per cubic foot; B = breadth of ditch at top of pipe, in feet; and H = height of fill, above top of pipe, in feet.

A NEW DESIGN IN BOILER SETTINGS

A modification of the usual horizontal tubular boiler setting is described in a recent bulletin issued by the Travelers' Indemnity Company, of Hartford, Conn.

The two distinctive features of the setting are the furnace arch A , and the air duct B , admitting secondary air through the bridge wall. In the ordinary form of setting for horizontal tubular boilers, the fire sheet of the shell, relatively very much cooler than the burning gases in contact with it, acts as a check upon combustion by its chilling effect and is itself subject to destructive strains. The deflecting arch, as shown by the sections, ends immediately back of the bridge wall, and the faces of fire brick are staggered to form projecting rings on its surface. This arch facilitates more satisfactory combustion of the furnace gases, and, in addition, distributes over the shell and tube surfaces the excess of work usually put upon the fire sheet. Both of these increase the efficiency of the boiler as well as add to its life. The arch must be carefully laid, with good blocks for

the end thrust, and segmental brick of the proper radius, with thin points of fire clay. If thus constructed, it will stand up under the high heat to which it is subjected.

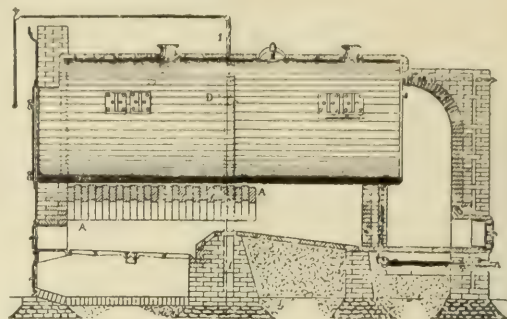


FIG. 1—VERTICAL LONGITUDINAL SECTION THROUGH BOILER SETTING

The auxiliary air supply to the hollow bridge wall enters through the duct B , controlled by the damper D ; to the transverse passage C , which has a clean-out door; and then up and

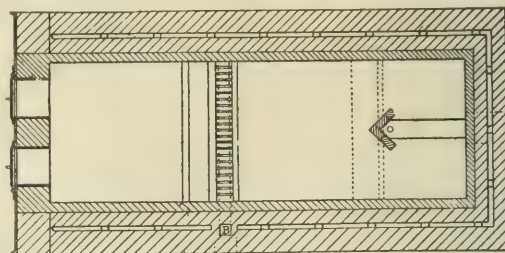


FIG. 2—HORIZONTAL SECTION THROUGH BOILER SETTING

out through $1/4$ -inch spaces between the fire brick in the crown of the bridge wall. The air is warmed by passage through the

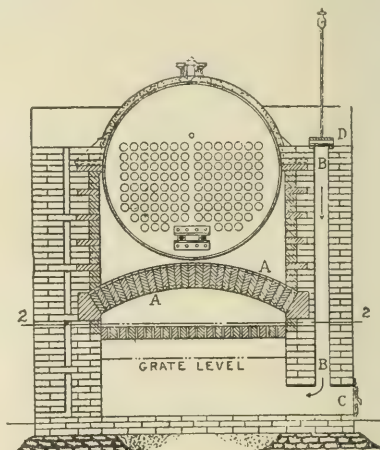


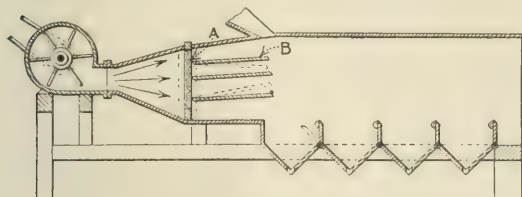
FIG. 3—SECTION THROUGH IGNITION ARCH

ducts, and is then introduced to the burning gases at what has been experimentally determined to be the best point for its admission.

A SEPARATOR FOR DRY MATERIAL

F. O. Stromberg, of Seattle, Wash., has devised an apparatus for the dry separation of ground ore, etc., which consists of a fan or other means of introducing an air blast, which passes

through a conical-shaped connection into a box, the bottom of which is divided into separate cone-bottomed receptacles. A screen is placed at the entrance of the box, shown at *A* in the drawing, for the purpose of creating eddies which will permit the greater part of the material to pass through the central slot formed by the movable partitions *B*. These partitions are adjustable and removable, and both the front and rear edges of each partition may be vertically independently adjusted. The arrows in the sketch show that the wind delivered from the fan passes into the inlet of the box and then expands slightly into strata or currents, the central one of which will pass along into and through the inlet without obstruction. Those currents which flow along the top and bottom of the box will set up eddies, as indicated by the fine arrows, and it is the purpose of these partitions to check the tendency to the formation of eddies



and to deliver the blasts of air into the box in several strata moving horizontally, and at equal speed. If these screen-panels are used with different meshes, an important bearing will be had upon the amount of air admitted through the slot or opening covered by that particular screen.

Power is applied to the fan which sets up a blast of air through the trunk and screen partition and throughout the length of the box to its outlet end. The material fed into the air-current encounters various strata of air which move at different velocities, according as the partitions have been set, and according to the mesh of the screen at the various openings; the larger pieces naturally offer more resistance to blasts of air than the smaller ones, and, therefore, the larger pieces will fall into the hopper nearest to the entrance of the long box, while the finer particles will fall into successive hoppers further along until the finest are discharged at the end of the box in the form of dust.

ABSORPTION AND REACTION TOWERS FOR CHEMICAL WORKS

Rudolf Heinz,¹ after reminding the reader that the main requirements for good absorption are greatest possible surface per cubic foot of filling, good mixing of gas, and the correct proportioning of the ratio between the section of the tower and the net section free for the passage of the gases, points out that the intending purchaser has a large variety of tower packings to select from. The days of coke as a filling material, except in certain very special cases, are numbered, and it has long been established that a small tower with good packing will accomplish the same amount of work as a large coke tower. Plain acid-proof bricks, prism-shaped bricks, triangular, rhomboidal, and trough-shaped bricks, and rings of various kinds, have all been tried in practice, and all have been found to have a common defect, namely, that they occupy a large percentage of the volume of the tower and leave insufficient "absorption space" for the gases.

Heinz states that the most successful tower packing of recent years were the "Guttman" hollow balls; the success of these was due to their very high "free space" (the percentage of the cubic capacity of a tower which remains free for gases). Millions of these balls were sold, but they could not come into general use on account of their high cost and because they were unsuitable for large towers and gases containing dust.

¹ *Z. anorg. Chem.*, **26**, No. 57, 419; see also *Chem. Trade J.*, **63**, 75.

The latest type of filling material, "Guttman" cells, are stated to be superior to even hollow balls, not only in regard to efficiency, but also because the cells are cheaper and possess a very high "free space." As shown in the illustrations (Figs. 1 and 2), these cells, when built up in a tower, form in section a regular honeycomb structure, each four cells enclosing a reaction space corresponding to an additional cell. The whole of the tower is thus symmetrically divided up into a number of equal reaction spaces, and in such a manner that both the outer and inner surfaces of the cells are wetted, and must be traversed by the gases which are ascending and diffusing through the tower filling. The formation of separate streams of liquids or gases cannot occur when these cells are used. Fig. 1 shows diagrammatically four cells arranged in the same manner as if they were stacked in a tower, the path of the liquid being

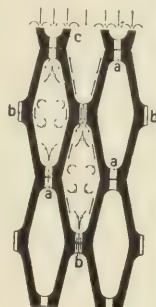


FIG. 1

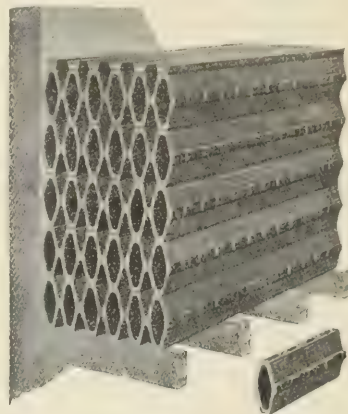


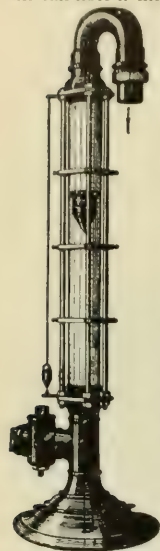
FIG. 2

indicated by plain arrows and the probable course of the gases by means of circled arrows. Slots (*a*) are made in the top and bottom walls of the cells; the gases entering from below expand in the interior of the cell, and pass out through the slots at the top. Each cell is provided at the sides with a number of projections (*b*), which rest against corresponding projections on the neighboring cells, and, at the same time, form the slots for the reaction space formed by four adjacent cells. The side walls of the cells being very steep, render it practically impossible, Heinz claims, for solid matter to collect on them, while, if necessary, the cells may be readily and quickly flushed down and cleaned. For extremely dusty gases—such, for example, as pass through a Glover tower—the lower third of the tower may be filled with large slabs or bricks in the usual way. The "active surface" of the large cells is 15 square feet per cubic foot, and of the small cells 30 square feet per cubic foot, and they are said to be designed and proportioned in every way to give the best results.

THE ROTAMETER

The "Rotameter" is a new instrument which indicates the volume of gas or liquid consumed per hour. It does not, however, measure absolute quantities like an ordinary gas meter or voltmeter, but gives the force of the gas current. It is based upon the following principle: The gas current which is to be measured flows through a vertical glass tube, the inside diameter of which increases continuously from the bottom to the top. Inside the glass tube is a conical float which rises to a certain height when gas is flowing through the former. The lift of the float depends upon the velocity of the gas or upon the volume of gas going through the tube in an hour, minute or second. On the float is a notched cylindrical rim. The gas, shooting through these notches, rotates the float like a Segner waterwheel, and

this rotation always keeps it in a vertical position and prevents friction on the wall of the tube. On the body of the float is a white, spiral line, which makes visible its quick rotation, and thus one can note if the meter is working or not.



The glass tube is graduated on the outside, and the calibration is obtained empirically, since its interior cannot be made with absolutely uniform slope. The scale on the glass tube may be made to read directly in cubic feet per hour (minutes or seconds) or in millimeters. In the latter case, tables are furnished with the meter for the determination of the exact volume of gas in cubic feet flowing through the meter. The instrument works as follows:

The float is lifted by the gas until the power which forces the gas current past it—i. e., the loss of pressure at that point—is equal to the weight of the float; or, in other words, the float is lifted so high that it leaves an opening between itself and the inside wall of the tube which allows the gas to flow through with a drop in pressure equal to the weight of the float.

The reading of the meter depends, of course, upon the density of the gas, as a denser gas, for the like loss in pressure requires a larger area for the passing of the same amount of gas. It, therefore, lifts

the float higher and gives an apparently larger reading than a lighter gas.

Rotameters are adapted to measure, regulate and control the quantity (or the velocity) of gases in pipe lines. They are installed directly in the line. The smallest current will, it is claimed, lift the float at once and hold it at a height corresponding or proportional to the velocity of the gas in the line. The scale on the outside of the glass tube gives directly the quantity of gas per hour (minute or second).

AN AUTOMATIC ELECTRIC DRYING OVEN

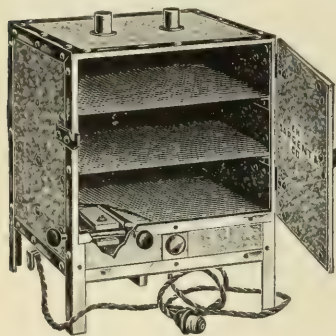
A drying oven, said to be practical and inexpensive, and designed especially to meet the requirements of the industrial

chemist, is being marketed by Messrs. E. H. Sargent & Co., of Chicago, Ill. It is shown in the accompanying illustration.

Electrically heated and automatically controlled, the claim is made that the oven may be set for any desired heat above room temperature and under 160° C. Under proper conditions, the manu-

facturers state, it will maintain that temperature within 1° C.

The oven has as much working space as the ordinary 10-inch \times 12-inch single copper wall oven, it does not occupy any more space, and it may be easily moved from place to place. It has a working space 10 inches high, 12 inches wide and 10 inches deep, and is provided with 2 shelves. The heating device with the thermostatic control is located in the base of the oven, a locking device is provided to insure against an accidental movement of the control mill-head on the outside, and there is a peep-hole for observing the heating coils. The manufacturers state that each unit of the heating element is easily accessible and replaceable



in case of injury, without the employment of tools or the dismounting of the whole heating element. Adjustable ventilation is provided to facilitate drying. The current consumption is very small, and the oven may be operated from an ordinary lamp socket.

A number of these ovens, which are constructed of asbestos composition bound with metal, have been installed for practical trial; the manufacturers report that no complaint has been received.

THE MINERAL PRODUCTION OF SWEDEN

The official report of the Swedish mineral output for 1912 shows the following (*Eng. Min. J.*, 96, 507, 510):

There were 6,700,556 metric tons of iron ore produced. Of this amount, 5,945,394 tons were considered first-class. The Swedish iron works consumed for the entire production of iron 43,219,576 hectoliters of wood charcoal; 359,584 tons of coal, 136,472 tons of coke; and, for the production of ingots, 337,321 metric tons of pig iron and 212,143 metric tons of scrap iron. The average Swedish blast furnace produces 20.07 metric tons of pig iron per day.

There were also mined the following ores in metric tons: zinc, 50,036; silver-lead, 2,877; iron pyrites, 31,835; manganese, 5,101; copper, 3,059. The metal production, excluding iron, was as follows: copper, 3,957 metric tons; zinc, 3,228; lead, 1,072 metric tons; silver, 961 kg.; gold, 30 kg. Other products and by-products of the mineral industry were: zinc sulfide, 33,522 metric tons; copper sulfate, 870; feldspar, 34,305; quartz, 22,365; alum, 144; ferrous sulfate, 335; graphite, 79; and powdered pyrolusite, 62 metric tons. All figures are arranged in the order of descending value.

THE PRODUCTION OF CALCIUM CARBIDE

It is reported that the world's production of calcium carbide is increasing. According to statistics published in *Chemical News*, 108, 106, it reached 300,000 tons in 1912. In Europe, Germany is the principal consumer of carbide. In 1911, 37,000 tons were imported, and in 1912 the importations amounted to 48,000 tons; no exportations were reported. Sweden produces the largest quantity of calcium carbide and consumes the least. The factories at Odda are capable of producing 80,000 tons per annum. In 1912, Switzerland exported calcium carbide valued at \$1,000,000; Austria-Hungary exports about 11,000 tons per year; England imports only between 14,000 and 18,000 tons; while France imported 3,302 tons and exported 6,225 tons in 1912. It is especially the development of lighting by acetylene in the French colonies which has increased so regularly the exports of carbide.

PROGRESS OF THE ELECTRIC STEEL INDUSTRY

A list of electric furnaces in operation by steel manufacturers in the United States is given in *Iron Age*, July 10, 1913.

Seven of these furnaces are of the Héroult design and include that of the Halcomb Steel Co., Syracuse, N. Y., a five-ton furnace producing tool steel; the Firth-Sterling Steel Co.'s furnace at McKeesport, Penn., of the same size and producing the same material; another belonging to the same company and at the same place, 2½-ton size, also producing tool steel; the Illinois Steel Co., Chicago, Ill., 15-ton capacity, producing rails; the American Steel & Wire Co., Worcester, Mass., 16-ton, producing wire rods; National Malleable Castings Co., Sharon, Penn., 3-ton capacity, producing castings; Treadwell Engineering Co., Easton, Penn., 2-ton capacity, also producing castings.

Of the Girod design there is the one-ton tool-steel furnace of the Simonds Manufacturing Co., Lockport, N. Y.; the Bethlehem Steel Co., South Bethlehem, Penn., a 10-ton tool-steel furnace; the 3-ton furnace, producing castings, of the Washington Iron Works, Seattle, Wash., and the 5-ton castings furnace of the

Portland Bronze & Crucible Steel Foundry, Portland, Ore. The Hering design includes the $\frac{1}{2}$ -ton castings furnace of the Niagara Steel Castings Co., Buffalo, N. Y., and the $\frac{1}{2}$ -ton tool-steel furnace of the Firth-Sterling Steel Co., McKeesport, Penn. The 2-ton castings furnace of the Crucible Steel Castings Co., Lansdowne, Penn., is of the Roechling-Rodenhauser design, while the $\frac{3}{4}$ -ton castings furnace of Deere & Co., of Moline,

ELECTRIC FURNACES BY COUNTRIES

Countries	Number	Countries	Number
Germany.....	34	Spain.....	1
Italy.....	20	Mexico.....	4
England.....	16	Canada.....	3
France.....	13	Japan.....	1
Austria.....	10	Brazil.....	1
Sweden.....	6		
Russia.....	4	Total, foreign.....	121
Belgium.....	3	United States.....	19
Norway.....	3		
Switzerland.....	2	Grand total.....	140

Ill., is of the Kjellin type. The $\frac{1}{2}$ -ton castings furnace of the Buchanan Electric Steel Co., Buchanan, Mich., is of the modified Stassano design, and the $\frac{1}{2}$ -ton furnace of the Crucible Steel Castings Co., Milwaukee, Wis., together with the $\frac{1}{2}$ -ton castings furnace of the Chicago Electric Castings Co., are designed by the Metallurgical Engineering Co., Chicago, Ill. The 1-ton special steel furnace of the Harrow Spring Co., Kalamazoo, Mich., is of the Greene induction type. The accompanying table shows the installations of electric furnaces by countries.

IRON CASTINGS TO RESIST CORROSION

The *Canadian Engineer*, July 17, 1913, states that some practical rules laid down by the American Foundrymen's Association for obtaining castings resistant to corrosion are the following:

(1) Use white iron if possible (white irons are especially useful where any acidity is to be encountered); (2) if it is not practicable to use white iron castings, chill those surfaces which are to be in contact with corrosive solutions; (3) if gray iron must be used, obtain dense, close-grained castings through the use of steel scrap or otherwise; (4) avoid oxidized metal, using pig irons of good quality, together with good cupola practice; and (5) keep the sulfur as low as possible. If possible, use deoxidizing agents, such as titanium or vanadium.

THE PRODUCTION OF FINISHED STEEL IN 1912

The Bureau of Statistics of the American Iron and Steel Institute in a special bulletin issued August 7th, announced complete statistics of the production of iron and steel merchant bars, concrete bars, skelp, nail plate, hoops, bands and cotton-ties, sheet piling, etc., in the United States in 1912; also statistics of the production of all kinds of finished rolled forms.

PRODUCTION OF FINISHED ROLLED IRON AND STEEL BY STATES
(Gross tons)

STATE AND SUBDIVISIONS	1912	1911
Maine, Mass.....	193,401	157,448
R. I., Conn.....	81,410	73,788
New York.....	1,034,071	768,763
New Jersey.....	175,143	154,563
Pennsylvania.....	12,254,040	9,426,827
Del., Virginia.....	32,888	30,487
Maryland.....	284,617	264,222
West Va.....	591,333	472,177
Ky., Tenn., N. C., Ga., Tex.....	192,737	187,149
Alabama.....	532,247	356,609
Ohio.....	4,330,487	3,382,063
Indiana.....	1,873,906	1,156,411
Illinois.....	2,253,664	1,939,350
Mich., Wis.....	246,991	148,285
Missouri.....	82,883	68,961
Kan., Colo., Wash.....	438,622	407,314
Ore., Cal.....	58,401	44,754
Total.....	24,656,841	19,039,171

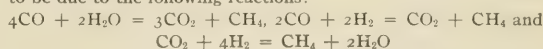
The bulletin shows the following totals for 1912 of all kinds of finished rolled forms of iron and steel, etc., with the production of similar articles in 1911, in gross tons:

ROLLED IRON AND STEEL	1911	1912
Rails.....	2,822,790	3,327,915
Plates and sheets.....	4,488,049	5,875,080
Nail and spike plate.....	48,522	45,331
Wire rods.....	2,450,453	2,653,553
Structural shapes.....	1,912,367	2,846,487
Merchant bars.....	3,047,362	3,697,114
Bars for concrete work.....	258,741	274,332
Skelp, flue, etc.....	1,980,673	2,446,816
Long angle splice bars, etc.....	(a)	571,772
Hoops.....	225,074	270,007
Bands and cotton ties.....	342,810	587,395
Sheet piling.....	22,827	22,276
Railroad ties.....	39,197	41,396
All other finished rolled.....	1,169,191	1,187,108
Rolled forg. blms. and billets.....	231,115	462,476
Exports blooms, billets, etc.....	(a)	347,783
Total.....	19,039,171	24,656,841

(a) Statistics not collected in 1911.

THE COMPOSITION OF WATER GAS

Vignon (*Compt. rend.*, 156, 1995) confirms the observation of Clement and Desormes and of Langlois that water gas always contains some methane. Investigation has shown that the formation of the methane is due to the presence of calcium oxide in the coke used. Experiments on the action of steam at 1000° on mixtures of coke and lime showed that the percentage of methane in the water gas increased with increasing proportions of lime. The formation of the methane is considered by Vignon to be due to the following reactions:



The lime is said to act as a catalyst in these reactions.

THE PAPER INDUSTRY OF AUSTRIA-HUNGARY

Paper, September 10, 1913, reports that new features have marked the close of the business year of the Austro-Hungarian paper industry.

This is particularly the case as regards the arrangements for uniform prices and terms. In this matter the example of the German Association seems to have been followed.

The Balkan troubles seem to have exercised a special effect upon the Austrian paper industry, of which the Balkan territory had long been special outlet. Among the measures of a social-political order, to which the attention of the association has been directed, was the question of resting from work on Sundays and the prohibition of juvenile night work. The question of the increased cost of wood and other raw materials had engaged the attention of the Government in connection with the augmented difficulty of procuring supplies. The proposed imposition of an export duty on rags had also been much discussed on the same lines as have marked that proposal in Germany. Another question of importance has been the revision of commercial treaties with foreign nations.

According to the statistics of production issued by Herr Franz Kramany the figures show in 1912:

	Tons
Paper of all kinds.....	424,785
Board of all kinds.....	49,521
Wood pulp.....	258,036
Cellulose.....	292,195
Bleached straw pulp.....	2,762
Total, 1912.....	1,027,299
Total, 1911.....	981,740
Total, 1910.....	954,036
Total, 1909.....	893,856

SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY—FORTY-EIGHTH MEETING, ROCHESTER, SEPTEMBER 8-12, 1913

PROGRAM OF PAPERS

GENERAL MEETINGS

Industrial Research in America. President's Address. A. D. LITTLE

Copper Covered Steel: Properties and Uses of the Composite Metal Made by Welding together Copper and Steel. (Illustrated.) JAMES O. HANDY

The Physical Chemistry of Photographic Development. C. E. KENNETH MEES

The Patent Expert and the Chemical Manufacturer. BERNHARD C. HESSE

The Utilization of Sewage. GEORGE A. SOPER.

In Commemoration of the Centennial of the Publication of the Berzelian System of Symbols. HENRY LEFFMANN.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

H. E. BARNARD, *Chairman*

GLEN F. MASON, *Secretary*

1. Bouillon Cubes: Their Composition and Food Value. FRANK C. COOK.

2. A Refractometer for Sugar Determinations. H. E. HOWE.

3. Hydrolysis of Starch. EDWARD GUDEMAN.

4. Lime Sulfur-Lead Arsenate Spray Mixture. W. E. RUTH.

5. The Commercial Utilization of Glucose and Glycerine in Modern Breads. O. G. MARCKWORTH.

6. Sulfur Dioxide in Gelatine. (Illustrated.) PAUL PORTSCHKE.

7. Solubility of Casein in Dilute Acids. L. L. VAN SLYKE.

8. The Effect of Rain on the Value of Hay. J. A. LE CLERC.

9. The Acid Content of Fruits. (Illustrated.) P. B. DUNBAR

AND W. D. BIGELOW.

10. Estimation of the Lime Requirements of Soil. J. A. BIZZELL

AND T. L. LYON.

11. The Valuation of the Lime-Sulfur Spray as an Insecticide.

H. V. TARTAR.

12. The Effects of Raw Materials on the Chemical Composition of American Beer. L. M. TOLMAN AND J. G. RILEY.

13. Food Standards and their Effect upon Food Law Enforcement. FLOYD W. ROBISON.

14. The Analysis of Maple Products. II. A Comparative Study of the Delicacy of Methods. J. F. SNELL AND J. M. SCOTT.

BIOLOGICAL CHEMISTRY SECTION

CARL L. ALSBERG, *Chairman*

I. K. PHELPS, *Secretary*

1. The Presence of Histidine-like Bodies in the Pituitary Gland (Posterior Lobe). (Preliminary Communication.) T. B. ALDRICH.

2. The Mutual Action of Pepsin and Trypsin. J. H. LONG.

3. A Further Study of the Well Water of Delaware, Ohio. G. O. HIGLEY.

4. Comparison of the Observed and Computed Heat Production of Cattle. H. P. ARMSBY.

5. On the Distribution of Mercury Following Acute Bichloride of Mercury Poisoning. JACOB ROSENBLUM.

6. The Non-interference of Ptomaines with Certain Tests for Morphine. JACOB ROSENBLUM AND S. ROY MILLS.

7. Notes on the Result of the Electrolysis of Witt's Peptone and Whole Protein. JAMES P. ATKINSON.

8. The Non-Development of Cytolytic Sera Following the Intravenous Injection of Mold Spores. R. A. GORTNER AND A. F. BLAKESLEE.

9. The Occurrence of a Toxin in the Bread Mold, *Rhizopus nigricans*. R. A. GORTNER AND A. F. BLAKESLEE.

10. The Effect of Acids upon the Catalase of Taka-Diastase. RAY E. NEIDIG.

11. Polyatomic Alcohols as Sources of Carbon for Molds. RAY E. NEIDIG.

12. Cleavage of Benzoylalanine by Mold Enzymes. ARTHUR W. DOX AND W. E. RUTH.

13. The Importance of Food Accessories as Shown by Rat Feeding Experiments. FRANK C. COOK.

14. The Influence of Various Organic Substances upon the Secretion of Diastase by Certain Fungi. C. F. CHAPMAN AND W. C. ETHERIDGE.

15. The Role of Oxidases in the Curly Dwarf Disease of Potatoes. H. H. BUNZEL.

16. A Time Recorder for Kymograph Tracings. OLIVER E. CLOSSON.

17. Apparatus for Studying Oxidases. OLIVER E. CLOSSON.

18. A Method for Studying Slight Degrees of Glycosuria, Adapted from Macleod and S. R. Benedict. AMOS W. PETERS AND MARY E. TURNHILL.

19. A Method of Estimating Fat in Infant Stools. W. S. HUBBARD AND D. M. CORVIE.

20. Nature of Humus and its Relation to Plant Life. S. L. JODINI.

21. The Estimation of Protein, Amino and Nucleic Acids in Potable Waters. PHILIP ADOLPH KOBER.

22. Surface Tension in Muscle Contraction. WM. M. BERG.

23. The Estimation of Raffinose by a Modified Biological Method. C. S. HUDSON AND T. S. HARDING.

24. The Elimination of Zinc. WM. SALANT AND JOHN B. RIEGER.

25. The Absorption and Fate of Tin in the Body. WM. SALANT AND ERNEST L. P. TREUTHARDT.

26. The Fate of Protein Digestion Products in the Body. D. D. VAN SLYKE.

27. The Configuration of Some Heptoses. GEORGE PIERCE.

28. Vanillin in Wheat, and its Relation to Soil. M. X. SULLIVAN.

29. Some Organic Constituents of the Culture Solution and the Mycelium of Molds from Soil. M. X. SULLIVAN.

30. A Method for the Determination of Small Amounts of Fat. W. R. BLOOR.

31. Nitrogenous Hydrolysis Products of Several Phosphatids. C. G. MACARTHUR.

32. Fatty Acids from Kephalin. L. V. BURTON AND C. G. MACARTHUR.

33. A Metabolism Experiment with Swine: (a) Mineral Requirements and Paths of Excretion; (b) The Balance of Acids and Bases; (c) The Relation of Magnesium and Calcium Metabolism; (d) Creatinine Excretion by Swine; (e) Anomalies in Digestion Coefficients. E. B. FORBES.

34. The Fate of Creatine and Creatinine when Administered to Rabbits. V. C. MYERS AND M. S. FINE.

35. Studies in the Comparative Physiology of Purine Metabolism. ANDREW HUNTER, M. H. GIVENS AND C. M. GUION.

36. Estimation of Protein, Amino and Nucleic Acids in Potable Waters. P. O. KOBER.

37. The Acidity of the Urine. H. D. HASKINS.

38. Metabolism Studies of Five Cases of Endarteritis Obliterans. MAX KAHN.

39. Calcium Content of Tuberculous Lungs. MAX KAHN.

40. Metabolism Studies of Two Cases of Amaurotic Idiocy. MAX KAHN AND A. HYMANSON.

41. Further Studies of Edema. T. L. HARKEY.

42. A Study on the Influence of External Hemorrhages on the Partition of Urinary Nitrogen. OLIVE G. PATTERSON.

43. Biochemical Studies of Selenium. VICTOR E. LEVINE.

44. Pigments Produced from Thymol by Ammonium Hydroxide. BENJAMIN HOROWITZ AND W. J. GIES.

45. A Differential Stain for Mucine and Mucoids. LOUIS BERMAN AND W. J. GIES.

46. The Origin and Significance of Salivary Sulfocyanate. MAX KAHN AND W. J. GIES.

47. Biochemical Studies of Dental Caries. A. P. LOTHROP AND W. J. GIES.

48. Further Studies of the Permeability of Lipin-Collodion Membranes. W. J. GIES.

49. The Physical and Chemical Constants of a Number of Monarda Fistulosa Oil. E. N. DAANE AND EDWARD KREMERS.

50. The Water and Volatile Oil Content of the Leaves of Monarda Fistulosa. NELLIE WAKEMAN AND EDWARD KREMERS.

51. Light and Health. W. D. BANCROFT.

FERTILIZER CHEMISTRY DIVISION

PAUL RUDNICK, *Chairman*

J. E. BRECKENRIDGE, *Secretary*

1. Chairman's Address. Fertilizer Chemistry. A Report of Progress. PAUL RUDNICK.

2. On the Use of Alundum Crucibles in the Determination of Phosphoric Acid. L. A. WATT AND W. T. LATSHAW.

3. The Analysis of Complete Fertilizers Containing Cyanamid. H. W. HILL AND W. S. LANDIS.

4. On the Preparation of Neutral Ammonium Citrate Solution. PAUL RUDNICK AND W. L. LATSHAW.

Report of Committees

Committee on Nitrogen. PAUL RUDNICK.

Committee on Phosphoric Acid. G. A. FARNHAM.

Committee on Potash. J. E. BRECKENRIDGE.

Committee on Phosphate Rock. F. B. CARPENTER.

Committee on Fertilizer Legislation. F. B. CARPENTER.

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

G. D. ROSENGARTEN, *Chairman*S. H. SALISBURY, JR., *Secretary*GEO. P. ADAMSON, *Vice-Chairman, Presiding*

1. The Protection of Iron and Steel by Paint Films. NORMAN A. DUBOIS.
 2. Some Tests of Paints for Steel Subjected to Alternate Exposure to Air and Fresh Water. (Illustrated.) PERCY H. WALKER and S. S. VOORHIES.
 3. The Effect of Resens on Soap Solutions. CHARLES H. HERTY and C. W. WILLIARD.
 4. Isoprene from Commercial Turpentine. CHARLES H. HERTY and J. O. GRAHAM.
 5. The Milling of Wheat and Testing of Flour. HARRY McCORMACK.
 6. A New Design of Coke Oven and a New Method of Coking. HARRY McCORMACK.
 7. The Electrolytic Reduction of Iron for Permanganate Titration. H. C. ALLEN.
 8. A Method for the Determination of Magnesium in Calcium Salts. J. C. HOSTETTER.
 9. Methods for the Examination of Natural Gas for the Production of Gasoline. E. S. MERRIAM.
 10. The Condensation of Gasoline from Natural Gas. GEORGE A. BURRELL and FRANK M. SEIBERT.
 11. Some Experiments on the Conversion of Long Leaf Pine to Paper Pulp by the Soda and Sulfate Processes. SIDNEY D. WELLS.
 12. Jerusalem Self-burning Limestone. CHARLES P. FOX.
 13. Improved Burner for Laboratory Use. CHARLES P. FOX.
 14. The Correlation of Chemical, Structural, and Thermal Analyses of Steels. J. CULVER HARTZELL.
 15. If the Chemist Manufactured Cotton-seed Meal. E. L. JOHNSON.
 16. The American Petroleum Society. IRVING C. ALLEN.
 17. Flash Testing. IRVING C. ALLEN.
 18. Alum Specification Report. W. M. BOOTH.
- Report of the Committee on Coal Analysis and Discussion. Led by W. A. NOYES.

ORGANIC CHEMISTRY DIVISION

TREAT B. JOHNSON, *Chairman*WILLIAM J. HALE, *Secretary*

1. The Structure of Urushiol, a Component of Japanese Lac. E. KOHMANN and TREAT B. JOHNSON.
2. The Reactions of Both the Ions and the Non-ionized Forms of Acids, Bases and Salts. S. F. ACREE.
3. The Existence of Mandelic Aldehyde in Aqueous Solution. WILLIAM LLOYD EVANS and C. R. PARKINSON.
4. The Mechanism of the Rearrangements of Dihydro- β -Naphthoic Acids. C. G. DERICK and O. KAMM.
5. Researches on Purines. xii: 2-Oxy-6-methyl-9-ethylpurine; 2-Oxy-6,8-Dimethyl-9-ethylpurine; 2-Oxy-6-methyl-8-thio-9-ethylpurine; 2-Methylmercapto-6-oxy-8-thiopurine; 2-Oxy-6-methyl-9-ethylpurine-8-thioglycolic Acid. CARL O. JOHNS and EMIL J. BAUMANN.
6. Researches on Purines. xiii: 2,8-Dioxy-1,6-dimethylpurine; 2,6-Dioxy-3,4-dimethyl-5-nitropyrimidine (α -Dimethyl-nitrouracil). CARL O. JOHNS and EMIL G. BAUMANN.
7. Acyl Derivatives of *o*-Aminophenol. J. H. RANSOM and A. NELSON.
8. Diacetyl: A Study in Structural Chemistry. W. M. BLANCHARD.
9. The Determination of Phenol in the Presence of Formaldehyde and Hexamethylenetetramine. L. V. REDMAN, A. J. WEITH and F. P. BROCK.
10. The Rate of Reaction between Hexamethylenetetramine and Phenol. L. V. REDMAN, A. J. WEITH and F. P. BROCK.
11. Synthetic Resins in Lacquers and Varnishes. L. V. REDMAN, A. J. WEITH and F. P. BROCK.
12. A New Synthetic Resin. L. V. REDMAN, A. J. WEITH and F. P. BROCK.
13. Synthetic Resins Produced by the Anhydrous Reaction between Phenols and Hexamethylenetetramine. L. V. REDMAN, A. J. WEITH and F. P. BROCK.
14. Chairman's Address. The Practical Utility of Hinsberg's Reaction. TREAT B. JOHNSON.
15. An Anomalous Reaction of Resorcinol. EDWIN F. HICKS.
16. The Action of Phthalic Anhydride on Benzene in Presence of Aluminium Chloride. F. B. ALLAN and C. R. RUBIDGE.
17. *o*-Benzoyl-benzoyl Chloride and *o*-Benzoyl-benzoyl Cyanide. F. B. ALLAN and H. C. MARTIN.
18. The Oleoresins of Jeffrey and Singleleaf Pines. A. W. SCHORGER.
19. The Leaf Oil of Douglas Fir. A. W. SCHORGER.
20. The Condensation of Thiourea with Acetylacetone. WILLIAM J. HALE.

PHARMACEUTICAL CHEMISTRY DIVISION

B. L. MURRAY, *Chairman*F. R. ELDRED, *Secretary*

1. Chairman's Address. Legislation Affecting Pharmaceutical Chemistry. B. L. MURRAY.
2. The Determination of Mercuric Iodide in Tablets. A. W. BENDER.
3. The Insecticidal Value of Fluid Extract of Larkspur Seed. J. B. WILLIAMS.
4. The Ferric Alum Estimation of Casein. H. V. ARNY and H. H. SCHAEFFER.
5. Some Physico-chemical Considerations in Reference to Inhalation Anaesthetics. CHARLES BASKERVILLE.
6. Amyl Nitrite, its Preparation, Purity and Tests. F. O. TAYLOR.
7. The Chemico-legal Interpretation of the U. S. Pharmacopoeia. LOUIS HOGREFE.
8. The Chemistry and Properties of Glycerophosphates. GASTON DUBOIS.
9. Purity of Chemicals and Quality of Vegetable Drugs during 1912. A. R. L. DOHME and H. ENGELHARDT.
10. Spirit of Nitrous Ether. H. ENGELHARDT and O. E. WINTERS.
11. The Composition of the Fruit of the Virginia Creeper. *Ampelopsis quinquefolia*. GEO. O. BEAL and EDW. A. GLENZ.

PHYSICAL AND INORGANIC CHEMISTRY DIVISION

S. L. BIGELOW, *Chairman*R. C. WELLS, *Secretary*

1. Observations on the Electrochemical Behavior of Minerals. R. C. WELLS.
 2. Fluidity and the Law of Mass Action. EUGENE C. BINGHAM.
 3. The Solubility of Water in Hydrocarbons. E. C. MCKELVY and F. A. WERTZ.
 4. Electrolysis of Solutions of the Rare Earths. (Illustrated.) L. M. DENNIS and B. J. LEMON.
 5. Action of Light on Copper Sulfate Solution. WILDER D. BANCROFT.
 6. Catalysis of Acetic Acid. WILDER D. BANCROFT.
 7. The Critical Solution Temperature and its Use in the Estimation of Moisture. E. C. MCKELVY.
 8. The Analysis of Basic Lead Sulfates. GEORGE A. PERLEY and G. F. LANE.
 9. Variations in the Compositions of Minerals. EDGAR T. WHERRY.
 10. The Increase in the Oxidizing Potential of Dichromate Ion on Platinum Caused by Certain Reducing Agents: An Improved Method for the Electrometric Titration of Ferrous Salts. GEORGE SHANNON FORBES and EDWARD P. BARTLETT.
 11. Equilibrium in the System Pyridine, Silver Nitrate and Water. W. S. HUBBARD.
 12. New Precipitants for Copper. PHILIP ADOLPH KOBER.
 13. The Electrochemical Equivalent of Iodine and the Value of the Faraday. E. W. WASHBURN and S. J. BATES.
 14. The Reduction of Chromium Chloride. H. C. P. WEBER.
 15. Electrolysis of Solutions of Sodium Hydrazide in Anhydrous Hydrazine. T. W. B. WELSH.
 16. Anhydrous Hydrazine as a Solvent. T. W. B. WELSH and H. J. BRODERSON.
 17. Chemical Reactions in Anhydrous Hydrazine. T. W. B. WELSH and H. J. BRODERSON.
 18. Electrolysis of Silver Trinitride in Liquid Ammonia. A. R. HITCH.
 19. Thermal Decomposition of Various Trinitrides. A. R. HITCH.
 20. The System Hydrazine Trinitride, Hydrazine. H. E. RIEGER.
 21. Action of Various Oxidizing Agents upon Hydrazine in Liquid Ammonia Solution. W. J. MARSH.
 22. Critical Phenomena in Binary Systems. FRITZ FRIEDRICH.
 23. The System Ammonium Sulfate, Ammonia. FRITZ FRIEDRICH, A. E. HOULEHAN and L. J. ULRICH.
 24. The System Mercuric Chloride, Ammonia. FRITZ FRIEDRICH.
 25. The System Ammonium Iodide, Ammonia. L. J. ULRICH.
 26. The System Ammonium Chloride, Ammonia. G. J. FINE.
 27. The System Copper Sulfate, Ammonia. G. J. FINE.
 28. The System Silver Trinitride, Ammonia. A. S. YOUNT.
 29. The Structure of the Trinitride Radicle. J. W. TURKENTINE.
- SYMPOSIUM ON PHOTOGRAPHIC CHEMISTRY
30. Direct Photographic Positives. GEO. E. PERLEY.
 31. Practical Sensitometry. P. G. NUTTING.
 32. Some Applications of Quantitative Absorption Spectroscopy in Chemistry. S. E. SHEPPARD.
 33. The Latent Image. W. D. BANCROFT.
 34. Theory of Developer. W. D. BANCROFT.
 35. Some Notes on the Cylindrical Acetylene Flame as a Standard of Light. L. A. JONES.

16. The Sensitiveness Curves of Photographic Plates Exposed to X-Rays. OREM TUGMAN.

17. The Theory of the Acid Fixing Bath. A. C. McDANIEL.

RUBBER CHEMISTRY SECTION.

D. A. CUTLER, *Chairman*

DORRIS WHIPPLE, *Secretary*

- Chairman's Address. Crude Rubber. D. A. CUTLER.
- Some Refinements of the Ignition Method for the Determination of Rubber in Vulcanized Goods. G. H. SAVAGE.
Discussion of Committee Reports.

WATER, SEWERAGE AND SANITATION SECTION

EDWARD BARTOW, *Chairman*

H. P. CORSON, *Secretary*

- Manganese in Illinois Waters. EDWARD BARTOW AND H. P. CORSON.
- The Comparative Value of Pure Calcium and Magnesium-calcium Lime for Water Softening. EDWARD BARTOW AND CLARENCE SCHOLL.
- Ventilation of the Schools of New York City. (Illustrated.) CHARLES BASKERVILLE.
- Winkler's Method for the Determination of Oxygen in Water: the Effect of Nitrite and its Prevention. FRANK E. HALE AND W. MELIA.
- The Determination of Sulfur in Certain Culture Media. H. W. REDFIELD AND C. HUCKLE.
- A Comparative Study of Methods for Determining Sulfur in Peptone. H. W. REDFIELD AND C. HUCKLE.
- The Value of Testing for Hydrogen Sulfide Production in the Bacteriological Examination of Potable Waters. E. M. CHAMOT.
- A Study of the Best Conditions for Hydrogen Sulfide Production in Peptone Media. E. M. CHAMOT AND H. W. REDFIELD.
- The Influence of the Composition of Carbohydrate Culture Media on the Amount and Character of the Gases Formed by Fecal Organisms. E. M. CHAMOT AND R. C. LOWARY.
- A Study of the Stokes Neutral Red Reaction. E. M. CHAMOT AND C. M. SHERWOOD.
- Further Notes on Standards of Potable Waters. J. CULVER HARTZELL.
- The Determination of Minute Amounts of Sulfur Dioxide in Air. A. SEIDELL AND P. W. MESERVE.
- The Quantitative Use of the Spectroscope in Water Analysis. W. W. SKINNER AND W. D. COLLINS.
- Comparison of Methods for the Determination of Dissolved Oxygen. W. W. SKINNER AND J. W. SALE.
- Longevity of *B. Typhosus* in Water. F. L. RECTOR.

AMERICAN ELECTROCHEMICAL SOCIETY. DENVER MEETING

The Twenty-fourth General Meeting of the American Electrochemical Society took place at Denver, Colorado, September 9-11, 1913.

PROGRAM OF PAPERS

- The Shape Factor. IRVING LANGMUIR.
- Simultaneous Determination of Copper and Lead, with the Rotating Anode. A. J. WHITE.
- Rapid Refining of Copper with a Rotating Cathode. C. W. BENNETT AND C. O. BROWN.
- The Heat Resistivity of Graphite and Carbon. J. W. RICHARDS.
- Effect of Light on Decomposition Voltage. ALAN LEIGHTON.
- The Art of Electric Zinc Smelting. W. McA. JOHNSON.
- Possible Applications of the Electric Furnace to Western Metallurgy. D. A. LYON AND R. M. KEENEY.
- The Transformation of Radiant into Chemical Energy. S. C. LIND.
- Electric Smelting of Chromium, Tungsten, Molybdenum and Vanadium Ores. R. M. KEENEY.
- The Carnotite Industry. SIEGFRIED FISCHER.
- Some Aspects of Heat Flow. E. F. NORTHRUP.
- The Electrolysis of Cyanide Solutions. E. F. KERN.
- The Electrolysis of Aqueous Solutions of the Simple Alkaline Cyanides. G. H. CLEVINGER AND M. L. HALL.

11. Some Observations on Base Metal Thermocouples. O. L. KOWALKE.

15. Osmium-Platinum. F. ZIMMERMAN.

16. The Electric Zinc Furnace. P. E. PETERSON.

17. Solid Thick Deposits of Lead from Lead Acetate Solutions. F. C. MATHERS.

18. Progress in Electrostatic Ore Dressing. F. S. MACGREGOR.

Sessions for the reading and discussion of papers were held at the Shirley Hotel, Denver; the University of Colorado, Boulder; the Colorado School of Mines, Golden; and on the top of Pike's Peak.

Trips to various points of interest, both technical and geographical, were included in the program. Among the plants visited were the following:

Sulton, Steele & Steele Co.: Experimental mill and testing plant. Dry process of ore concentration; electrostatic separation of sulfide minerals.

Western Chemical Manufacturing Co.: Manufacture of acids, anhydrous ammonia, and liquid carbonic acid, concentration of mixed sulfide ores, magnetic separation, producer-gas power plant.

Henry E. Wood Ore Testing Co.: General testing of ores, concentration, flotation, cyanidation, magnetic separation.

United States Mint: Electrolytic refining of gold.

American Zinc Ore Separating Co.: Testing plant, electrostatic, separation, dry jigging, separation of complex ores.

American Smelting & Refining Co.: Lead smelting, Huntington-Heberlein and Dwight-Lloyd sinter roasting, bag-house recovery of smelter fume.

Screenless Sizer Co.: McKesson-Rice screenless sizing of ores, crushed rock and coal.

THE CHEMICAL SOCIETIES IN NEW YORK CITY

PROGRAM OF MEETINGS FOR THE SEASON 1913-1914. SESSIONS IN RUMFORD HALL, CHEMISTS' CLUB

American Chemical Society, October 10, 1913.

Society of Chemical Industry, October 24, 1913.

American Chemical Society, November 7, 1913.

Society of Chemical Industry, November 21, 1913.

Joint Meeting, American Chemical Society, December 12, 1913.

American Chemical Society, January 9, 1914.

Society of Chemical Industry (Perkin Medal), January 23, 1914.

Joint Meeting, American Electrochemical Society, February 6, 1914.

American Chemical Society (Nichols Medal), March 6, 1914.

Society of Chemical Industry, March 27, 1914.

Society of Chemical Industry, April 24, 1914.

American Chemical Society, May 8, 1914.

Joint Meeting, Society of Chemical Industry, May 29, 1914.

American Chemical Society, June 5, 1914.

OBITUARY—EUGENE A. BYRNES

The death of Dr. Eugene A. Byrnes occurred on August 1st, at Haven, Maine, where he had gone for a vacation.

Dr. Byrnes was born in New York State in 1862. He had graduated from the University of Michigan, and in 1884 became a teacher in the Central High School, Washington, D. C. Subsequently he entered the Examining Corps of the United States Patent Office, and rapidly rose to the position of Chief of a Division. In the meanwhile he graduated from the Law School

of Columbian University, and was admitted to the Bar. He also took a post-graduate course leading to the degree of Ph.D. in Electro-chemistry and Physics. In 1901 he resigned his official position and entered upon the practice of law with Mr. C. P. Townsend as a partner. Later Mr. J. H. Brickenstein entered the firm, the three constituting the well-known firm of patent lawyers, Brynes, Townsend and Brickenstein.

Dr. Byrnes was a member of the American Chemical Society, American Electro-Chemical Society, American Institute of Electrical Engineers, Chemists' Club of New York City, Society of Chemical Industry, Patent Law Association of Washington, and of the Cosmos and Chevy Chase Clubs of Washington.

OBITUARY—F. H. DANIELS

Fred H. Daniels, Chairman of the Board of Engineers of the United States Steel Corporation, Chief Engineer of the American

Steel and Wire Company, and President of the Washburn and Moen Company, died at his home in Worcester, Mass., on August 31, 1913, after a long illness.

Mr. Daniels, who was born in 1853, had been very prominently identified with the development of the iron and steel industries for 40 years, and over 150 patents, a number of which revolutionized processes of manufacture, indicate his activity.

Mr. Daniels supervised the erection of plants for the American Steel and Wire Company at Waukegan, Ill., Cleveland, O., San Francisco, Cal., and Birmingham, Ala. He was one of the board of consulting engineers who designed the United States Steel Corporation's plant at Gary, Ind., and served in a similar capacity at the time of the erection of the Duluth mills of the Minnesota Steel Company.

In 1900, the Paris Exposition Jury of Awards bestowed a gold medal on Mr. Daniels as "celebrateur," and in 1909, he was decorated by King Oscar of Sweden.

W. A. HAMOR

NOTES AND CORRESPONDENCE

ON METHODS OF ANALYSIS OF CRUDE GLYCERINE

Editor of the Journal of Industrial and Engineering Chemistry:

From the recital of difficulties given by E. A. Ray in *THIS JOURNAL*, 5, 784, it is evident that there is some confusion existing as to the exact procedure of the International Standard Method for glycerine analysis.

The glycerine sub-committee of the American Chemical Society met at London in 1910, with the British Expert Committee and representatives from Germany and France and agreed on the following: (see report of the American Committee, *THIS JOURNAL*, 3, 679). The British report is identical.

INSTRUCTIONS FOR CALCULATING THE ACTUAL GLYCERINE CONTENT

(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylizable impurities if present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol.

This is the official method at present in use in the United States. Nothing is said about any allowance nor is there a limit set at 2.5 per cent organic residue at which or below which the chemist is prohibited from making a correction for acetylizable impurities.

The British *Executive Committee*, a committee of British Soap Manufacturers, appended a recommendation to the report of the Expert Committee as follows:

RECOMMENDATIONS BY EXECUTIVE COMMITTEE

If the non-volatile organic residue at 160° C. in the case of a soap lye crude be over 2.5 per cent, then the residue shall be examined by the acetin method and any excess of glycerol found over 0.5 per cent shall be deducted from the acetin figure.

This recommendation was not signed by the British Experts and was rejected by the American Committee as being arbitrary and unscientific. Residues of 2.5 per cent and below often give very material corrections for impurities. Even if this correction is small there is no reason why it should not be made nor is there any clear reason why the limit should be set at 2.5 per cent rather than at 1, 2 or 3 per cent. It is the chemist's task to determine the actual glycerine present to the best of his ability and leave all questions of allowance and limits to others.

English crudes purchased under these conditions of sale as laid down by British manufacturers will of course be tested

with these limitations, but there has been no such custom with regard to American crudes, which have been bought and sold on the basis of the American Chemical Society report.

Referring to the instructions for calculating the glycerine content it will be seen from (2) that the determination of the organic residue is not required. It may be obtained by determining the ash and deducting this from the total residue. This determination is not needed when glycerine alone is being looked for and the chemist who has been asked to analyze a sample for glycerine by the International method is within his rights in declining to state the per cent of organic residue or ash unless he receives additional compensation therefor. There would seem to be little excuse, however, for a chemist to refuse to state the total residue and the correction as found, these determinations being necessary before the true per cent of glycerol can be ascertained.

The difference between the tests of the referee and seller amounting to 1.38 per cent might easily be due to the presence of solid salt in the samples or to the deposition of salt after the crude had left the seller's factory. The accurate sampling of crude glycerine if salt has separated is next to impossible and chemists may differ 5 per cent and more on very salty crudes.

Doubtless the crude referred to by Dr. Ray is free from solid salt or he would have called attention to its presence. It is a fact, however, that it is the exception rather than the rule to find a delivery of American soap lye crude entirely free from deposited salt. If manufacturers of crude would give their product ample opportunity to cool and settle in tanks before filling out into drums the fundamental cause for most of the dissatisfaction with glycerine analysis would be removed.

A. C. LANGMUIR

Chairman Sub-Committee on Glycerine Analysis

September 8, 1913

WHAT'S THE MATTER WITH THE AMERICAN CHEMIST?

Editor of the Journal of Industrial and Engineering Chemistry:

Judging from the answers one reads to the above question, Mr. Chemist is fast arriving. Some of the answers are amusing, some dramatic, and there are lamentation and pathos in others. The plaintiffs seem to be actuated by disposition, by training, by fitness, or by sarcasm. Surely, Mr. Chemist will come out of the crucible thoroughly refined at the end of the heat; but it seems to me that we are losing sight of viewpoints and are failing to differentiate between pure science and applied science.

Science is the study and correlation of phenomena and their

interpretation, together with the formulation of laws. We have abstract science and we have concrete science. The former is not concerned primarily with matter; but the latter is. Chemistry lies between the two, and might be termed an abstract concrete subject. Then we have pure chemistry and applied chemistry, and at the foundation of all work in chemistry we find *analysis*. All chemists are analysts of greater or less degree, depending upon the extent of their training, experience, and innate qualities. To speak in disparaging language of the *analyst* or the *analytical chemist* is to reproach the great and good men in the profession of chemistry, past and present. Such terms as "has-been" and "would-be" need no comment, except to say that it is far better to be a "good-old-has-been" than "a never-was" or "a never-will-be."

Then there is the term *research*. What does it mean? Is it a going after a nebular something floating about in the cosmos of chemistry? Some seem to think so, and such chemists I should term research chemists devoting their time and ability to pure chemistry *per se*. We shall always need such men; but these men must have private fortunes, or must be provided with funds by others. We need patrons of recluses. The work of the recluse is invaluable, and should be encouraged; but he must not forget the Latin phrase *per aspera ad astra*.

However, there is another meaning to *research*. Perhaps the word *inquiry* defines it. With this definition in mind, I should say that there is the research chemist who is searching along synthetical lines by means of analytical methods for the purpose of producing a given product, which product he has produced by abstract reasoning, for a given purpose. That is to say, the *end product* to be is predetermined, and its measure of value when found is *applicability*.

Research men fall naturally into one of the above categories; but some are so endowed as to fit either. Then again some fit one or the other by adaptability, an extremely valuable asset. Hence, we have two genera and four species of research chemists.

In considering the industrial phase of research chemistry, we are confronted with the fact that the manufacturer is not engaged in business as a recreation or as a philanthropic enterprise, but for the purpose of producing remunerative products. The German manufacturer does not employ a research chemist from *per se* motives; but for what he will or hopes to get from *results*. There is no lack of money in Europe or America or Canada or Mexico for the research man who can "deliver the goods;" but everybody fights shy, financially, of him who cannot present a reasonable demonstration of his ability to *find out* by *inquiry* through *research* some method to reduce cost or increase production or both, just as he fights shy of the novice in chemistry. High ambition and lofty ideals are right and just and commendable; but they are by no means confined to the research chemist in pure science *per se*. This type of chemist might and may bring about the results desired by the manufacturer, and we wish him every success and encouragement; but he is too great a risk for the manufacturer who is looking for an industrial research chemist. If the industrial research chemist is treated as a hireling, he is himself largely a fault, and the thing for him to do is to stop "kicking against the pricks" if he wishes to occupy a higher plane, and there are many up there to-day.

Perhaps I have been unfortunate in my professional dealings with research men and various enterprises for the past twenty odd years, and perhaps I "see through a glass darkly;" but I am convinced that "by their works ye shall know them," the research men in industrial chemistry.

J. CULVER HARTZELL

BLUE ASH, OHIO
September 11, 1913

ON CALCULATING THE FAT-FREE RESIDUE OF MILK

Editor of the Journal of Industrial and Engineering Chemistry:

In *Chem. Abst.*, 7, 2444, under "Foods," there is given a formula

proposed by H. M. Höyberg for "Calculating the Fat-free Residue of Milk" $[(V + F)/4 = \text{fat-free dry residue}]$, *Skand. Vet. Tidskrift*, 1912, 259-62; *Deutsch. tierärztl. Woch.*, 21, 253.

It appears that the above formula was first suggested by Dr. S. M. Babcock as long ago as 1891 in the Eighth Annual Report of the Wisconsin Experiment Station for the year ending June 30, 1891, page 298. Dr. Babcock writes the formula $(L + F)/4 = \text{solids-not-fat}$, in which $L =$ the Quevenne lactometer reading.

The Quevenne lactometer reading $= V$ in Höyberg's formula since both $=$ "a figure obtained by subtracting unity from the specific gravity and placing the decimal point after the first two numerals (neglecting 0)."

During the year 1907, while comparing the per cent of solids of a very large number of chemical analysis of milk with the results secured by using different formulas for calculating the solids-not-fat after determining the Quevenne lactometer reading and the per cent of fat by the Babcock method, I noticed that when the per cent of fat was added to the Quevenne reading and the sum secured was divided by 4, the quotient equaled very closely the per cent of solids-not-fat secured by the chemical method. Then I developed the formula $(L + F)/4 =$ the per cent of solids-not-fat. Before going further, I looked up the work done by others along this line and found that the formula was suggested by Dr. Babcock as stated above.

In 1909, along with other formulas commonly used, this one was published in the book: "Questions and Answers on Milk and Milk Testing," p. 68, by C. A. Publow and H. C. Troy, Orange Judd Company.

The formula is very simple and easy to apply and since three different chemists, working independently, have developed it and find it to give accurate results, it appears that it should have a permanent place in practical milk inspection and factory work where it is necessary to secure an approximately correct composition in the shortest possible time.

HUGH C. TROY

N. Y. STATE COLLEGE OF AGRICULTURE
CORNELL UNIVERSITY, ITHACA
September 18, 1913

NOTE ON COLORIMETRIC METHOD FOR TITANIUM IN IRON AND STEEL

In describing the procedure for determining titanium in steel when less than 0.02 per cent is present (THIS JOURNAL, 5, 735), I referred to the importance of conducting the ether separation so as to have small and nearly constant amounts of iron in the acid solutions. This essential condition is best attained by carrying out the ether separation in the following manner:

Cool the concentrated ferric chloride solution, pour into the separatory funnel, and wash with hydrochloric acid (2 parts strong acid : 1 part water) until the volume amounts to 25 cc. Add 50 cc. alcohol-free ether, agitate thoroughly, and allow to stand for five minutes after the two solutions have separated. Draw off the acid solution, avoiding the ether solution entirely even though a slight loss of acid solution may be necessary to do so. These precautions insure a greatly reduced and practically constant amount of iron in the acid solution.

CHAS. R. McCABE

LIMA, OHIO
Sept. 19, 1913

PETROLEUM PRODUCTION IN 1912

GAIN OF TWO MILLION BARRELS

The great production of petroleum in 1911, which was 220,449,391 barrels, was equaled and passed in 1912, when the total reached 222,538,604 barrels. Higher prices were the rule in 1912 except in California, and even in that State there was no material decline. The total value therefore increased markedly,

reaching \$164,087,342, or 22.41 per cent above the value for 1911.

The greatest increase in quantity was in California, where the total advanced from 81,134,391 to 86,450,767 barrels, a gain of 5,316,376 barrels, or 6.55 per cent. Wyoming showed the remarkable gain of 742 per cent, from 186,695 barrels to 1,572,306 barrels, owing to the increased activity of the Mid-West Oil Co. and the Wyoming Oil Fields Co. Operations in northern Texas also more than offset the usual decline in the Gulf region and resulted in a significant gain for the State.

INCREASED EXPORTS

The volume of crude oil and of all the usual products exported from the United States increased, owing to the fact that foreign conditions were much more favorable to American exporters. Meanwhile the importation of gasoline from the East Indies was a favorable element in relieving the growing demand for this product on the Pacific coast.

DECREASED STOCKS

The improved conditions in the export trade and the increased capacity of the refiners to take care of the great yield of crude oil resulted in a marked decline in stocks in all fields except California, and even there the storage of petroleum was checked by an increase in consumption.

The total stocks of all crude oils at the beginning of 1912 aggregated 138,000,000 barrels. By the close of the year they had declined to 125,000,000 barrels, a decrease of about 10 per cent. The decline was greatest in the fields east of the Rocky Mountains, where on January 1, 1912, the stocks aggregated 94,000,000 barrels; they were reduced during the year to 79,000,000 barrels, a decrease of about 16 per cent.

This decline at once brought out a marked stimulation of prices all over the East, with a view to increasing the activity of drilling. Its effect was so marked, that the natural decline of the older fields was checked. Even Ohio showed a slight increase in production in 1912, for the first time in 12 years.

The total production by States is given below:

QUANTITY AND VALUE OF PETROLEUM PRODUCED IN THE UNITED STATES AND THE AVERAGE PRICE PER BARREL IN 1912

STATE	Quantity (barrels)	Value	Average price per barrel
California.....	86,450,767	\$ 39,213,588	\$0.454
Colorado.....	206,052	199,661	0.973
Illinois.....	28,601,308	24,332,605	0.851
Indiana.....	970,009	885,975	0.913
Kansas.....	1,592,796	1,095,698	0.688
Kentucky.....	484,368	424,842	0.877
Louisiana.....	9,263,439	7,023,827	0.758
New York.....	874,128	1,401,880	1.604
Ohio and Michigan.....	8,969,007	12,085,998	1.347
Oklahoma.....	51,852,457	34,957,612	0.674
Pennsylvania.....	7,837,948	12,886,752	1.644
Texas.....	11,735,057	8,852,713	0.754
Utah.....	1,572,306	798,470	0.507
Wyoming.....	1,572,306	798,470	0.507
West Virginia.....	12,128,962	19,927,721	1.643
Total for 1912.....	222,538,604	164,087,342	0.737
Total for 1911.....	220,449,391	134,044,752	0.608

GOVERNMENT CONTROL OF CHILEAN MINERAL DEPOSITS

Consul Alfred A. Winslow, Valparaiso, reports that much interest is taken in the law just passed by both branches of the Chilean Congress which suspends the old mining code indefinitely, and which really means much for the future of Chile, since the mineral resources are its greatest attraction for foreign capital. It is understood that this is a result of heavy investments of American capital in copper and iron ore properties during 1912 and 1913, which will represent an expenditure of \$15,000,000

to \$20,000,000 when the respective plants have been completed. The new law provides that: (1) During the time the right of individuals to denounce iron mines is suspended, the State shall be authorized to make the necessary declaration and inscription of such deposits. (2) Such claims to have the superficial dimensions decreed by the President of the Republic, and possession to be taken in the usual way provided in case of individuals by the mining code, though the State shall not be obliged to start work within the term laid down in such cases. (3) The rights thus acquired by the State shall be in perpetuity, and no license or other rates shall be paid. (4) The mensuration and establishment of titles to be undertaken by the mining section of the Direction of Public Works. (5) All iron mines the property of individuals, the rights to which shall lapse through non-payment of the necessary taxes, shall revert directly to the State and shall not be sold by auction as provided in the mining code. (6) The President of the Republic is authorized to establish the regulations necessary for carrying out this law.

The *South Pacific Mail*, of Valparaiso, states the case quite clearly from the viewpoint of the Chilean: "The present mining code considers all metals wherever found as the property of the State, but grants the privilege of denouncing and staking out claims to individuals. The recent discoveries of rich extensive deposits of iron ores suitable for export in their primitive form led to the filing of many claims, in the hope of being able to pass them on later to foreign capitalists. As large tracts of valuable State lands were thus being taken possession of by individuals who had no intention of themselves working the mines, but merely wished to clear a commission on their sale, the right of denouncing and staking out claims as regards iron ores was indefinitely suspended.

It is understood that Government surveyors have already determined the existence of vast deposits of iron ore. These deposits will now definitely become State property on the payment in the usual terms of the surface value of the ground in cases where the land is privately owned. Government will, therefore, be in position either of reserving these supplies against the time when smelting works have been established in this country, or of treating directly with foreign syndicates for working the ore; and in either case the treasury will reap the benefit formerly accruing to the person who first denounced the claims, a solution which must be considered a just one, in view of the fact that the surveys are being carried on at Government expense."

One American company has acquired extensive deposits of rich iron ore that it is proposed to ship to the United States in large quantities, beginning with the opening of the Panama Canal, which will place a large tonnage at the disposal of American interests who are after business in this part of the world.

SCOTTISH OIL FUEL FOR BRITISH NAVY

Winston Churchill, the British Lord of Admiralty, estimates a probable annual output of 400,000 to 500,000 tons of oil fuel from Scottish shale fields for 150 years to come, if necessary. It is announced that the present output is about 250,000 tons. An Edinburgh writer states that "Scottish shale oil has proved, by repeated and prolonged tests, to be highly suitable for the purposes of the Admiralty, which in turn has shown a lively appreciation of the importance of having a reliable supply of the new fuel within easy reach."

PROGRESS OF ARTIFICIAL-SILK INDUSTRY

Consul William H. Hunt, St. Etienne, France, reports that processes for producing artificial silk continue to multiply. New means of rendering the silk strong, supple, and brilliant are

constantly being discovered, and the industry has now attained a high degree of perfection.

The dry-weaving process, by which the solid thread is directly obtained, has replaced the use of coagulating liquids. In spite of this, nitrocellulose silk is disappearing from the market because it can not enter into competition with other artificial silks obtained by a simpler process and which are cheaper and more solid.

The first of these rival productions was obtained by dissolving cellulose in cupro-ammoniacal liquor. The difficulties encountered in this operation brought about the discovery of cellite, an acetyl cellulose, soluble in acetone, which might be employed for cinematograph films, being incombustible, were it not for its too great suppleness; it can be used for coating wood and metals for it does not crack. Another substance of the same nature is sericose, which is used for printing on calico.

The solidity of all artificial silks may be increased by treating them with formaldehyde, which operation is called "stheriosage."

The report just issued by La Soie Artificielle, Givet, discloses a net profit of \$201,100, against \$144,500 the previous year. The capital is \$289,500.

CLAY PRODUCTS INDUSTRIES IN THE UNITED STATES IN 1912

The great magnitude of the clay-working industry of the United States is shown in a chart just issued by the United States Geological Survey. It shows a total value for 1912 of \$172,811,275, an increase of \$10,575,094 over 1911. These products include the several varieties of brick, drain and other tile, sewer pipe, terra cotta, pottery, fire brick, and other clay products, the various building bricks representing the greatest value, with a total of \$73,425,819. The number of building bricks manufactured was 10,281,114,000.

Ohio led the States in the value of her clay products with an output amounting to \$34,811,508, or over one-fifth the total production for the United States. Pennsylvania was second, with a production valued at \$21,537,221; New Jersey third, with \$19,838,533; and Illinois fourth, with \$15,210,990. Eight states produced clay products in 1912 to a value exceeding \$5,000,000 and 26 states to a value exceeding \$1,000,000.

During 1912, pottery was produced to the value of \$36,504,164, the increased value of the output for 1912 over 1911 being almost \$2,000,000. Ohio was by far the largest producer in 1912, being credited with \$15,508,735, and New Jersey was next, with over \$8,000,000. Six states produced pottery to the value of more than \$1,000,000.

BOOK REVIEWS

Iron and Steel, an introductory text-book for engineers and metallurgists. By O. F. HUDSON, with a section on corrosion. By GUY D. BENGOUGH. New York: D. Van Nostrand Co. 173 pp., 8vo, illustrated. \$2 net.

This volume is one of a series entitled "Outlines of Industrial Chemistry," text-books, introductory to the chemistry of the national industries, edited by Guy D. Bengough, lecturer in metallurgy, Liverpool University. In the preface the author, who is lecturer in metallography, Birmingham University, states that the object has been to give the more important principles of the metallurgy of iron and steel in as short a manner as possible, omitting almost entirely the practical details of methods of production in order to lay more stress on the constitution of steel and cast iron and the effect of mechanical and heat treatment, corrosion being taken up in a special section. And the author has accomplished what he set out to do in a clear and concise manner, producing a very readable and interesting book for beginners.

The first chapter deals with the testing of iron and steel, stress being put on English methods; under impact tests, the Fremont machine might have been mentioned and under Hardness, the Shore scleroscope referred to.

The chapter on smelting of iron ores is rather short, the section on iron ores being poor; the magnetites of the Lake Superior district are emphasized, while the hematite deposits from the same locality are not mentioned. The description of the blast-furnace is rather too brief, and while the reactions in the upper part of the furnace are given at length, those of silicon, phosphorus, manganese and sulfur in the smelting zone are not given.

The brief description of the properties of cast iron is good, though the use of the word "eutectic" without a definition when describing the effect of phosphorus is probably an oversight.

The chapters on Foundry Practice, Malleable Cast Iron, Puddling, the Crucible, Bessemer and Open Hearth Processes are concise and clear. The statements that coke-fired crucible furnaces are most commonly used, that mild steel is not used for the charge, undoubtedly refer to English practice, for in this

country the regenerative furnace is almost exclusively used and "melting bar" forms the basis of most charges. The same applies to the statement that the basic open hearth is used principally for mild steel. The Duplex process seems worthy of description.

The section on the mechanical treatment of steel is also short and clear, as is that on the impurities in steel, though the statement that since iron sulfide is fluid at ordinary rolling temperatures, it gives rise to red-shortness, even in small quantities, will not be accepted by all.

The chapter on the Constitution of Iron Carbon Alloys is specially well written and illustrated by excellent photographs, while that on heat treatment is also good. Annealing and refining are not distinguished.

The description of special steels is very clear and well written. The space devoted to analyses of high-speed tool steels, however, might better be used for a page of analyses of alloy steels in general.

The chapters on Steel Castings and Case-hardening and Welding are also good.

Section II, eighteen pages of material dealing with the corrosion of iron and steel, is clearly written and very interesting, but could have been much condensed and yet brought within the scope of the rest of the book. A critical discussion of the relative corrosion of wrought iron and steel would have been very timely.

Taken as a whole, the book is a good one, is well written in a clear, concise manner, and while it is in places written from the British point of view, it contains the main principles of interest to the general reader who is beginning the study of Iron and Steel from the standpoint of the engineer. The make-up of the book, paper, printing, etc., are good, the reproductions of the photomicrographs being exceptionally clear and sharp.

WM. CAMPBELL

Metallic Alloys: Their Structure and Constitution. By G. H. GULLIVER. Second edition, revised, largely rewritten and greatly enlarged, 409 pages, 310 illustrations, 8vo. Price,

\$3.25 net. London: Chas. Griffin & Co., Ltd. Philadelphia: J. B. Lippincott Co.

This is a very decided improvement on the first edition which made its appearance in 1908, and contained but 254 pages and 104 illustrations.

To quote from the preface: "The book obviously is not intended as a guide to the practical manufacturer of alloys, except in so far as a knowledge of the equilibrium conditions, and the unstable conditions of mixtures is of assistance in regulating their composition and heat treatment. It is addressed mainly to engineers and to students of engineering who desire some knowledge of the minute structure of metals and alloys, and of the manner in which the structure develops and changes."

The contents are: methods of investigation, physico-chemical equilibrium of mixed substances; binary alloys in which no definite chemical compounds are formed; binary alloys which show evidence of the formation of definite chemical compounds; transformations which take place in completely solid metals and alloys; equilibrium conditions in metallic mixtures; the structure of metals and alloys; the bronze, the brasses, and other alloys of copper; steel and other alloys of iron; alloys of more than two metals; the microscope in engineering practice; 245 references to the literature, and a rather complete index.

After showing that alloys are solutions and discussing the various theoretical considerations of equilibrium, by reference to typical curves and diagrams, the author proceeds to the classification of binary alloys, treating each class first theoretically and then by means of existing cases. Considerable space is devoted to recrystallization.

The reviewer was pleased to note the author's treatment of imperfect equilibrium, especially the diagram. To quote: "The simpler conditions of imperfect equilibrium are of very frequent occurrence, and are of considerable practical importance, though difficult to investigate with any degree of exactness, because the constitution of the mixture must be always somewhat indeterminate." Textbooks usually omit careful reference to the condition so often noticed in rapidly cooled alloys, a good illustration of which is the changes in the positions of the vertical or nearly vertical boundary lines between the different fields of the commercial brasses.

The discussion of chilling, annealing and vibration is interesting. In this connection the very important subject of *pouring temperature* is touched upon. "In castings which are allowed to cool gradually in the mould, the length of time occupied in solidification depends upon the pouring temperature of the metal, and the material of which the mould is made. A low pouring temperature and a mould of high heat conductivity means a chilled casting, while a high pouring temperature and a mould of low conducting power will allow of only slow solidification, followed by a more or less effective annealing; heating the mould is equivalent to decreasing its conductivity." This is an extremely important phase of alloy work and it is unfortunate that so little work has been done along this line, due, of course, to the lack of suitable pyrometers. The author has not, however, entirely covered the literature on the subject.

The chapter on "steel, and other alloys of iron" is much more complete than is usual in elementary books of this kind.

The final chapter on "The Microscope in Engineering Practice" is of considerable interest and importance, particularly to an engineer.

In the discussion of methods of investigation one would have liked to see more space given to the subject of pyrometers and particularly to furnaces, which is dismissed with one short paragraph.

On page 194 we read "the addition of lead to brass reduces the size of the crystals," with a reference to "The Tensile

Strength of Copper-tin Alloys" by Shepherd and Upton, published in the *Journal of Physical Chemistry*, June, 1905. After a careful perusal of this reference the reviewer fails to find such a statement. Indeed the statement is in error, as lead up to about 1 per cent has very little effect upon brass, while in greater quantities it segregates in tiny globules, diminishing, of course, both the strength and ductility of the metal. If it reduced the size of the crystals the strength would thereby be increased, which is not the case.

On page 281 in the section on copper-aluminum alloys we read: "The only alloys of this series which have a commercial value are those containing more than 89 and less than 5 per cent of copper." And again on page 283, "it is not advisable to use more than 5 per cent of copper." These statements do not accord exactly with the facts, in actual practice, particularly in automobile work. While a copper-aluminum alloy, containing but 5 per cent of copper is used where a lower elastic limit is required, in crank cases requiring considerably more strength, an alloy containing 8 per cent copper is regularly used.

The book is clearly printed on good paper, the diagrams are clear and possess an excellent feature in that wherever several persons have worked upon a system, the results of all are plotted. The micrographs, the greater number of which have been prepared especially for this book, are very clear.

The references are assembled at the ends of the various chapters. This arrangement, the reviewer believes, is objectionable to the reader, unless he be unusually well acquainted with the book.

However, this book is an excellent elementary treatise and would make a very good addition to a library of one interested in alloys.

J. M. LOHR

Service Chemistry. By VIVIAN B. LEWIS AND J. S. S. BRAME. Fourth edition. London: Arnold; New York: Longmans. 1913, 8vo. Pp. 576 + xvi. Price, \$4.20 net.

This is essentially a work on industrial and engineering chemistry. It differs from the standard books of that class in two ways. It pays little or no attention to matters not coming under the professional notice of officers of the army or navy. On the other hand, it does not appear to assume previous knowledge of the principles of the science, for it includes an introduction to the principles, and brief conventional accounts of the common elements and their compounds are scattered through the book.

The industrial material seems to be well selected, and in many instances the topic is discussed in much more detail than we should expect in a single volume. Thus combustion (17 pp.) deals at length with charcoal and coal, their state of division, their tendencies to spontaneous ignition, adsorptive powers, and so forth. The impurities in water and boiler incrustation each occupy a whole chapter. The chapter on fuel (36 pp.) discusses calorific values and the ways of measuring them, liquid fuel and machinery for its injection by steam, pressure alone, and air; internal combustion engines, the various fuels they use and the relative efficiencies of these fuels. Nitric acid, niter, and explosives, their manufacture and behavior, receive much detailed attention (100 pp.). Iron and steel, in relation to their uses in the services, occupy a long chapter (50 pp.). Alloys are discussed in two chapters, and excellent diagrams make the theory clear in each case. Corrosion and the means of preventing it, and a descriptive list of pigments close the volume.

As a condensed treatise on certain branches of applied chemistry, the book is up to date and practical, and the discussion is critical and instructive. The many suggestive re-

marks, and valuable and appropriate bits of information that are continually encountered, show that the authors have given much thought to the needs of students preparing for naval or military service.

It cannot be said that the authors are so successful in handling the fundamental matters which lead up to these applications. A chapter on galvanic batteries immediately following that on hydrogen necessarily involves the mention of many substances and reactions which have not yet been reached. There is evidence that the authors understand how to apply modern views to chemical problems, but they are not pedagogically very successful in introducing those views in the systematic portions of the book. The modern ideas are introduced, but the discarded views remain side by side with them, in a way that must confuse the student-reader very much. Molecules repel each other (p. 9) although the kinetic theory is correctly used a little later. Nascent hydrogen seems to infest all kinds of galvanic cells alike, although the ionic theory is used in the same connection. The electromotive series of the metallic elements appears correctly, except for the omission of hydrogen. The bald rule of precipitation makes its appearance, but the equilibrium between ionogens in solution is given without any cross-connection in the next paragraph.

The whole discussion of molecular weight is vitiated by an old fallacy—that an atomic weight in grams of “any gaseous element” occupies 11.16 liters at 0° and 160 mm. What about the five inert gases; not to speak of ozone, and the vapors of phosphorus, mercury and many other elements?

The section headed “chemical behavior” of hydrogen says that “its chemical behavior is such that it is often theoretically looked upon as being the vapor of a metal.” This whole section should be clarified.

“The metallic elements end in *um*,” not their names. Split infinitives are too frequent.

Saturation, water of crystallization, and efflorescence require more than two sentences among them, for the sake of clarity. The next section, that on “water of hydration” should be redistributed. It is composed of one statement about the union of the oxides of metallic elements with water, one on the transition points of ice, water, and steam, one on the influence of water on climate, and one on the high specific heat of water.

The book could be used for reference in high schools and colleges. The more interested pupils would find in it much information on practical subjects, which are barely touched upon in the ordinary text books. The book is well printed and copiously illustrated.

ALEXANDER SMITH

Liquid Air—Oxygen—Nitrogen. By GEORGES CLAUDE. Translated by Henry E. P. Cottrell, with an afterword by the translator, and a preface by Dr. d'Arsonval. 418 pp. Published by Blakiston's Son & Co., Philadelphia. Price, \$1.50

Georges Claude is the enthusiastic experimenter who refused to let any difficulties, particularly the great one of lubrication of cylinders at low temperatures, keep him from accomplishing the production of liquid air by expansion of compressed air behind the piston. The story of his persistent endeavor to develop this process, as opposed to the Hampson and the Linde processes, and his final success in making it the most efficient one for producing liquid air, is told in this book. Notable as was this achievement, in Claude's mind it was only one step toward the cheaper separation of oxygen and nitrogen from the air and the development of their use in chemical industry, so the book tells also the advances made by the author in the separation of oxygen from air by partial condensation and in methods of rectification of liquid oxygen.

While the presentation of the author's own accomplishments in their proper scientific and historical setting is the main theme of the volume, the whole subject of the liquefaction of gases and

the separation of mixed gases by liquefaction and evaporation is quite fully set forth. The contents are in four parts: Part I on the elementary physics of the general subject and the historical steps from Faraday to the victory of Kamerlingh-Onnes over helium. This leads naturally into Part II, on the commercial liquefaction of air, in which both the theory and the practice are treated, particularly as to the relative advantages of the Linde process of expansion by simple outflow without useful work, on the one hand, and the Claude method of expansion with recoverable external work, on the other hand. Part III is an entertaining trio of chapters on the preservation and properties of liquid air. Part IV is on the separation of air into its elements, which is the commercially important process to which liquefaction is preliminary.

A detailed discussion of the various rectification processes of Linde, Levy, Heilbronner and Claude is given. For his latest machines, as manufactured by the *Société l'Air Liquide*, the author claims the possibility of separating 1.5 cu. m. of oxygen per horse-power hour.

Interesting throughout, Parts II and IV contain most valuable information for all who need to keep up with the progress of the liquid air and oxygen industry. It is to be regretted that there could not have been in the same volume a treatment of the remarkable accomplishment of Claude in the recovery by refrigeration of the vapors of volatile liquids which otherwise go to waste in many manufacturing operations.

The book, except in the more theoretical parts, is written in the style of the popular lecture, which has made it all the more difficult for the translator to conceal the fact that the book was written in French, rather than in English. Errors that appear in the text are amusing, rather than important.

GEORGE B. PEGRAM

Disinfection and Disinfectants. By M. CHRISTIAN. Physician in Chief, Royal Institute for Infectious Diseases, Berlin. Translated from the German by Charles Salter with eighteen illustrations. London: Scott, Greenwood and Son, 8 Broadway, Ludgate, E. C. 1913.

Any attempt to cover all aspects of the subject of disinfection and disinfectants within the compass of 100 pages would, of course, be a hopeless task, and the author of this little work has not made any such attempt. The volume confines itself substantially to a review of the fundamental principles underlying disinfection, together with a brief résumé of disinfectants in common use and apparatus used in their connection. A rather disproportionate amount of space is given to detailed descriptions of specific forms of the latter.

The book is divided into four chapters, the first of an introductory character, giving a general review of the methods of transmission of disease. The second chapter describes the principles and methods of disinfection by physical means, including dry heat, steam, hot liquids, light and other rays, and electricity. Chapter three takes up the subject of chemical disinfection, while Chapter four concludes with descriptions of combinations of systems of disinfection, together with illustrations and descriptions of specific apparatus.

The book being originally a German work which has been translated and published in England, the apparatus and methods described differ in many respects from those in use in this country. The whole work is elementary in its character and does not make any attempt to go deeply into the scientific aspects of the subject. The matter of testing the potency of disinfectants by laboratory tests is barely touched upon, the one method given being rather primitive in its character.

The book should prove a useful and interesting little manual for those whose work requires some knowledge of disinfection, but who have not the time or inclination to make a special study of the subject. The text is clear and free from typographical errors.

J. A. DECHUÉE

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian, Chemists' Club, New York

- Arsenic Compounds, Handbook of Organic.** By A. BERTHEIM. 8vo. Price, \$2.00. Ferdinand Enke, Stuttgart. (German.)
- Carbon.** By H. LE CHATELIER. 1. 8vo., pp. 324. Price, \$4.50. W. Knapp, Halle. (Translation.) (German.)
- Carbon in Organic Materials, A Simple Method for the Determination of.** By E. B. HART and K. J. Woo. *Journal of the American Chemical Society*, Vol. 35, 1913, No. 8, pp. 1056-1061.
- Chemistry, A Course in General.** By W. McPHERSON and W. E. HENDERSON. 8vo., pp. 556. Price, \$3.75. Ginn & Co., New York.
- Chemistry and Mineralogy, Elementary Course in.** C. I. ISTRATI and G. G. LONGINESCU. 8vo., pp. 402. Price, \$3.00. Librairie Gauthier-Villars, Paris. (French.)
- Colloids and their Viscosity.** By WOLFGANG OSTWALD, et al. 8vo. Price, \$1.75. Faraday Society, London.
- Cyanamid, Manufacture, Chemistry and Uses.** EDWARD J. PRANKE. 8vo., pp. 112. Chemical Publishing Co., Easton.
- Detonators and Electric Detonators, Investigations of.** By CLARENCE HALL and SPENCER P. HOWELL. 8vo., pp. 73. U. S. Bureau of Mines, Bulletin No. 59.
- Explosives, The Analysis of Black Powder and Dynamite.** WALTER O. SNELLING and C. G. STORM. 8vo., pp. 80. U. S. Bureau of Mines, Bulletin 51.
- Gas Analysis.** By L. M. DENNIS. 8vo., pp. 412. Price, \$2.25. Macmillan Co., New York.
- Glycerin, its Production, Use and Determination.** By SIEGFRIED W. KOPPE. 8vo., pp. 196. Price, \$0.75. A. Hartleben, Vienna. (German.)
- Hydrogenation, Catalytic.** By PAUL SABATIER. 8vo., pp. 20. Price, \$0.50. Akademische Verlagsgesellschaft, Leipzig. (German.)
- Industrial Poisoning from Fumes, Gases, and Poisons of Manufacturing Processes.** By J. RAMBOUSEK. 8vo., pp. 360. Price, \$3.25. Edward Arnold, London. (Translation.)
- Inorganic Chemistry, The Technique of Experimental.** By L. DOERMER. 4th ed. 8vo., pp. 1010. Leopold Voss, Leipzig. (German.)
- Inorganic Chemistry, Gmelin and Kraut's Handbook of.** III. Part 1. By C. FRIEDHEIM and F. PETERS. 7th ed. L. 8vo., pp. 1568. Price, \$17.50. Carl Winter, Heidelberg. (German.)
- Inorganic Chemistry, Handbook of Methods of.** Vol. III, Part 1. By ARTHUR STAHLER. 8vo., pp. 692. Price, \$6.00. Veit & Co., Leipzig. (German.)
- Iron, Contributions from the Iron Foundry Institute at the Technical High School of Breslau. I.** O. SIMMERSBACH. 8vo., Price \$3.50. Verlag Stahlseiden, Duesseldorf. (German.)
- Legal Chemistry.** By R. DE FORCRAND. 8vo., pp. 392. Price, \$1.75. Dunod & Pinat, Paris. (French.)
- Metallurgical Analysis, Quantitative.** By C. F. SIDENER. 8vo., pp. 110. Price, \$1.25. H. W. Wilson Co., Minneapolis.
- Metallurgical Practice, Hand. Vol. I.** By VARIOUS AUTHORS. 2nd ed. 8vo., pp. 490. Price, \$5.25. Chas. Griffin & Co., London.
- Oils and Fats, Examination of Hydrocarbon.** By D. HOLDE. 4th ed. 8vo., pp. 596. Price, \$4.50. Julius Springer, Berlin. (German.)
- Oils, Etheral. Vol. II.** By E. GILDEMEISTER. 2nd ed. 8vo., pp. 713. L. Staechmann, Leipzig. (German.)
- Organic and Inorganic Chemistry with Special Consideration of Bleaching, Dyeing and Finishing Processes.** By M. REIMANN. 4th ed. 8vo., pp. 374. M. Koch, Leipzig. (German.)
- Patents, Engineers' Handbook of.** By W. MACOMBER. 8vo., pp. 288. Price, \$4.00. Little, Brown & Co., Boston.
- Periodic Phenomena in Chemistry.** By R. KREMANN. 8vo., Price, \$1.25. Ferdinand Enke, Stuttgart. (German.)
- Petroleum Refining, Scientific Foundations of.** By L. GURWITSCH. 8vo., pp. 278. Price, \$2.25. Julius Springer, Berlin. (German.)
- Plant Products, An Introduction to the Chemistry of.** By PAUL HAAS and T. G. HILL. 8vo., pp. 400. Price, \$2.00. Longmans, Green & Co., New York.
- Smoke and Smoke Prevention, Bibliography of.** By ELLWOOD H. McCLELLAND. 8vo., pp. 164. Price, \$0.50. University of Pittsburgh, Pittsburgh.
- Sugar Factory, The Beetroot and the Beetroot.** By E. SAILLARD. 8vo. Price, \$1.00. J. B. Ballière et Fils, Paris. (French.)
- Thermodynamics, Introduction to.** By R. BLONDIOT. 8vo., pp. 102. Price, \$1.00. Th. Steinkopff, Dresden. (Translation.) (German.)
- Water Purification and Sewage Disposal.** By J. TILLMANS. 8vo., pp. 133. Price, \$2.00. Constable & Co., London. (Translation.)
- Ammonia and Nitrogen Determination.** By KNUBLAUCH. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 59, pp. 425-431.
- Analysis, The Graphical Method of Recording Results in.** By J. R. BLOCKEY. *Tanners' Yearbook*, 1913, pp. 103-111.
- Caoutchouc Resins.** By MARTIN KLASSERT. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 69, pp. 471-472.
- Catalysis in Organic Chemistry.** By JEAN NIVIERE. *Revue générale de Chimie pure et appliquée*, Vol. 16, 1913, pp. 189-196 and 220-224.
- Celluloid, Viscosity and its Importance for the Chemistry of, in Theory and Practice.** By H. SCHWARZ. *Zeitschrift fuer Chemie und Industrie der Kolloide*, Vol. 12, 1913, pp. 32-42.
- Cellulose, The Benzoyl Esters of.** By H. OST and F. KLEIN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 61, pp. 437-440.
- Cellulose, Studies on.** By EDWARD G. PARKER. *Pulp and Paper Magazine of Canada*, Vol. 11, 1913, No. 13, pp. 449-451.
- Chlorin Cells, The Billiter Alkali.** By A. J. ALLMAND. *Transactions of the Faraday Society*, Vol. 9, 1913, Nos. 1 and 2, pp. 3-10.
- Colloids and their Viscosity.** By WOLFGANG OSTWALD, et al. *Transactions of the Faraday Society*, Vol. 9, 1913, No. 1-2, pp. 34-107.
- Colors under Artificial Light, Aspect of.** By DAVID PATTERSON. *Cotton*, Vol. 77, 1913, No. 11, pp. 409-412.
- Combustion, Surface.** By JAMES A. SEAGER. *Steam*, Vol. 12, 1913, No. 3, pp. 70-71.
- Copper Refinery, The Great Falls Electrolytic.** By WILLIS T. BURNS. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 9, pp. 509-518.
- Corrosion of Iron and Steel.** By BERTRAM LAMBERT, et al. *Transactions of the Faraday Society*, Vol. 9, 1913, No. 1-2, pp. 108-139.
- Explosions of Coal Gas and Air, Some of the Conditions Affecting.** By E. L. SELLERS and C. CAMPBELL. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 14, pp. 730-736.
- Furnaces, Electric, their Design, Characteristics and Commercial Application.** By W. MCA. JOHNSON and GEO. N. SIEGER. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 9, pp. 504-507.
- Galvanotechnic, Progress in, in 1912.** By K. NEUKAM. *Zeitschrift fuer angewandte Chemie*, Vol. 26, 1913, No. 63, pp. 441-444.
- Lead, Contribution to the Study of the Actions of Various Waters upon.** By HARRI HEAP. *Journal of the Society of Chemical Industry*, Vol. 32, 1913, No. 15, pp. 771-775.
- Metal Analysis, Progress in, in 1912.** By TH. DOERING. *Chemiker Zeitung*, Vol. 37, 1913, No. 96, pp. 961-962.
- Nitroglycerin, Quantitative Separation of Nitrosubstitution Compounds from.** By A. L. HYDE. *Journal of the American Chemical Society*, Vol. 35, 1913, No. 9, pp. 1173-1182.
- Nitroglycerin, The Freezing of.** By HAROLD HIBBERT and G. PRESCOTT FULLER. *Journal of the American Chemical Society*, Vol. 35, 1913, No. 8, pp. 978-989.
- Oils, Differentiation of Animal and Plant.** By J. MARCUSSEON and H. SCHILLING. *Chemiker Zeitung*, Vol. 37, 1913, No. 100, pp. 1001-1002.
- Osmium.** By A. GUTBIER. *Chemiker Zeitung*, Vol. 37, 1913, No. 85, pp. 837-859.
- Patent Law, Scheme for a, Design Law and Trade-mark Law.** By KARSTEN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 61, pp. 433-437.
- Phosphate, The Manufacture of Acid.** By J. S. BROGDON. *American Fertilizer*, Vol. 39, 1913, No. 5, pp. 25-29.
- Portland Cement, A New Process of the Examination and Study of.** By B. GRUENWALD. *Chemiker Zeitung*, Vol. 37, 1913, No. 88, pp. 885-886.
- Potash, Possible Sources of, in the United States.** By FRANK K. CAMERON. *American Fertilizer*, Vol. 39, 1913, No. 1, pp. 25-32.
- Rubber Solutions, The Viscosity of.** By B. J. EATON. *India Rubber Journal*, Vol. 46, 1913, No. 7, pp. 17-19.
- Soap Powders, Investigation of.** By G. A. BRAGO. *Chemical Engineer*, Vol. 18, 1913, No. 2, pp. 73-76.
- Spectrum, Analysis, Quantitative.** By G. A. SHOOK. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 9, pp. 494-497.
- Starches, Methods of Testing.** By HAMBLEN BUEL. *Paper*, Vol. 12, 1913, No. 9, pp. 19-24.
- Sulfite Pulp Manufacture, Recovery of Acid in.** By NECAS. *Paper*, Vol. 12, 1913, No. 10, pp. 20 and 34.
- Sulfite Digesting Liquor, Tests for.** By GOESTA VON ZWIEBERGK. *Paper*, Vol. 12, 1913, No. 13, pp. 15-17.
- Sulfur Trioxide, Determination of, in Sulfur and Pyrite Roasting Furnaces.** By E. RICHTER. *Pulp and Paper Magazine of Canada*, Vol. 11, 1913, No. 13, pp. 445-447.
- Water, Lime Sterilization of.** By CHARLES P. HOOVER and RUSSELL D. SCOTT. *Engineering Record*, Vol. 68, 1913, No. 10, pp. 257-259.
- Water Purification.** By GEORGE W. FULLER, et al. *Engineering Record*, Vol. 68, 1913, No. 11, pp. 293-294.
- Wood, The Preservation of, by Cyanization.** By FRIEDRICH MOLL. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 67, pp. 459-463.

RECENT JOURNAL ARTICLES

- Acidity, The Electrometric Method for the Measurement of.** By LLOYD BALDERSTON. *Journal of the American Leather Chemists' Association*, Vol. 8, 1913, No. 9, pp. 370-378.
- Alloys, The Constitution of, and the Patent Law.** By W. GUERTLER. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 69, pp. 465-471.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

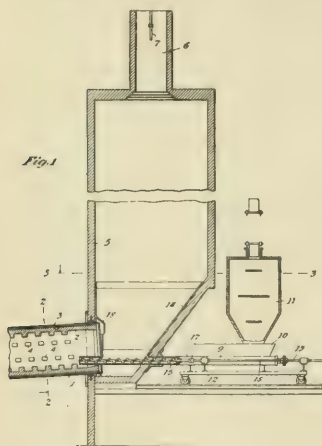
Manufacture of Oxalates. L. W. Andrews, June 24, 1913. U. S. Pat. 1,065,577. A mixture of sawdust and alkali is placed in a closed vessel. Superheated steam under low pressure is introduced into the vessel and heat is applied to the exterior of the vessel.

Purifying Vanadium. W. F. Blecher, June 24, 1913. U. S. Pat. 1,065,582. A lead salt is added to an acid solution containing vanadium and impurities. An alkaline carbonate is then added until lead vanadate is precipitated. This is treated with sulfuric acid, producing lead sulfate and an acid solution of vanadium free from impurities.

Cement-burning Kiln. T. A. Edison, June 24, 1913. U. S. Pat. 1,065,597. The

furnace is designed to effect economics in the fuel burned by reducing the temperature of the stack gases and to reduce the loss due to the carrying off of unburned material in the stack gases.

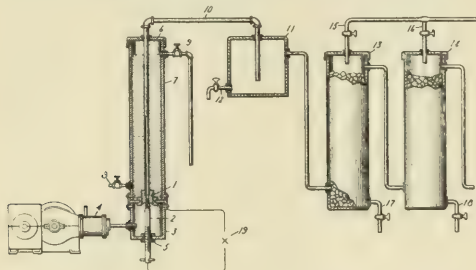
The rotary kiln tube connects with a settling chamber located at the base of the stack and a screw conveyor is arranged at the bottom of the settling chamber for returning to the kiln tube the material deposited in



the settling chamber.

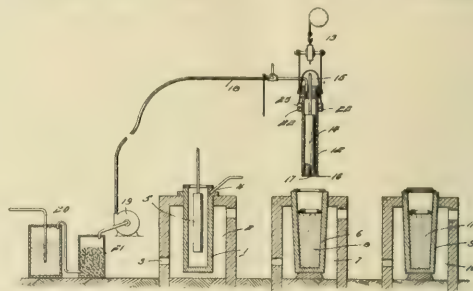
Removing Sulfur and Phosphorus from Iron and Similar Metals. A. E. Greene, June 24, 1913. U. S. Pat. 1,065,605. Lime is heated in an electric furnace and the resultant vapors withdrawn by suction and introduced into the body of the metal under treatment.

Chemical Reaction by means of an Electric Arc. J. L. R. Hayden, July 1, 1913. U. S. Pat. 1,066,272. A low-voltage high current arc is produced between the hollow electrode 1 and the adjustable electrode 2. The gaseous mixture to be acted upon is introduced into the chamber 3 by means of a blower



at a sufficient pressure to produce a high velocity gaseous current through the copper tube 6. The gases are acted upon while passing through the arc and are immediately cooled below the dissociation point of the product of the reaction by contact with the walls of the tube 6.

Producing Clad Metals. W. M. Page, July 1, 1913. U. S. Pat. 1,066,312. A billet of steel is first treated to give it a clean surface and then heated in an atmosphere of steam to produce a thin layer of oxid. The billet is then dipped into molten copper which causes the oxid and underlying carbon to react to produce pure iron with which the copper can unite. The billet with cohering film of copper is then removed, the manipulation



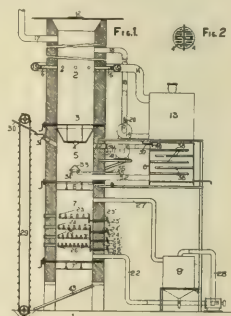
being conducted in an atmosphere of producer gas freed from carbon dioxide and oxygen.

Producing Citric Acid. B. Zahorski, July 1, 1913. U. S. Pat. 1,066,358. A culture of fungus *Sterigmatocystis nagra* is cultivated in a culture medium containing about 15 per cent of citric acid and a sugar solution is inoculated with the culture, the growth of the fungus being allowed to proceed in the solution to produce citric acid therein.

Producing Soluble Albumin Powder. R. Bass, July 1, 1913. U. S. Pat. 1,066,364. Cooked meat is hydrolyzed with ammonia and water at a temperature of 102° to 107° C. The temperature is reduced to 45° C. and calcium hydroxide is added. The temperature is then raised to 90° to 100° C. and soda lye is added after which the soda is neutralized with hydrochloric acid.

Hydrating Lime and Utilizing Heat of Hydration. H. L. Doherty, July 8, 1913. U. S. Pat. 1,066,719. In this process

limestone is charged into the top of the kiln and the lime produced passes into the hydrating chamber 5, where it is subjected to the action of current of air mixed with sufficient steam to hydrate the lime. The air, heated by the heat developed by the reaction, is divided into two currents, one passing up through the kiln in contact with the hot lime in the cooler 3, where it is further heated and then into the combustion zone 2, where it is used to burn the fuel. The other current is withdrawn by the blower 10 and forced, together with fresh air, through the evaporating chamber 8, where it takes up water. The steam laden air is then conducted into the hydrating chamber and passed through the lime, where the steam is utilized as described.



Manufacture of Camphor from Borneol or Isoborneol. C. Ruder, July 8, 1913. U. S. Pat. 1,066,758. A neutral solvent is added to a mixture of borneol and chromic acid in quantities such that the temperature does not rise above 25° to 30° C.

Refining Shellac, Etc. H. Cassard, July 8, 1913. U. S. Pat. 1,066,794. Shellac is subjected to the dissolving action of alcohol. There is then added a hydrocarbon solvent for the wax and the two solutions mixed homogeneously at a temperature above the melting point of the wax. The two solutions are allowed to settle in layers at this temperature and separated.

Smelting Iron Ores. F. M. McClenahan, July 8, 1913. U. S. Pat. 1,066,833. Aluminiferous iron ore is smelted in the presence of sodium chlorid as the fixing agent.

Producing Carbon or Lampblack. G. Fernekes, July 8, 1913. U. S. Pat. 1,066,894. A stream of methane is passed into a zone of sufficient temperature (above 1300° C.) to immediately dissociate the gas into carbon and hydrogen.

Making Fertilizer. O. K. Slater, July 8, 1913. U. S. Pat. 1,067,224. A mixture of slag and phosphatic minerals is softened and disintegrated by subjecting it to the action of steam under pressure. It is treated with sulfurous fumes while still moist and then acted upon by ammonia gas.

Varnishes. L. Meunier, July 15, 1913. U. S. Pat. 1,067,536. A concentrated solution of tannin in water is mixed with neutral sulforicinate of soda and highly rectified turpentine.

Manufacture of Formaldehyde. M. J. Kusnezow, July 15, 1913. U. S. Pat. 1,067,665. A mixture of methyl alcohol vapor and air is passed over heated metallic silver.

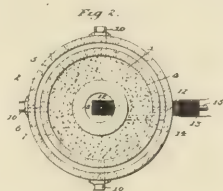
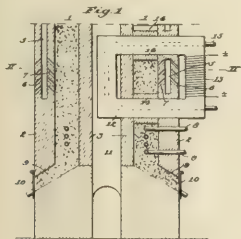
Non-Inflammable Cellulose Compound. W. G. Lindsay, July 15, 1913. U. S. Pat. 1,067,785. The composition contains acetyl cellulose in acetone, urea, triphenylphosphate and acetone.

Hydrogenated Fatty Food Product. C. Ellis, July 22, 1913. U. S. Pat. 1,067,978. This is a composition of lard-like consistency comprising hydrogenated corn oil of viscous consistency and an edible fatty material which may be hydrogenated cottonseed oil.

Manufacture of Malt. R. Wahl, July 22, 1913. U. S. Pat. 1,068,028. Lactic acid is added to malt during its manufacture.

Decomposition of Fats and Oils. B. E. Reuter, July 22, 1913. U. S. Pat. 1,068,079. Glycerides are decomposed into glycerin and acids by successively heating emulsions of the charge with different restricted portions of a sulfo-fatty acid catalyzer, each portion being insufficient to effect complete decomposition, and removing the aqueous solution of glycerin and spent reagent.

Treating Carbon and Apparatus Therefor. W. A. Smith, July 29, 1913. U. S. Pat. 1,068,707. The body of carbon or carbonaceous material to be treated is moved progressively through a heating zone established by causing induced currents



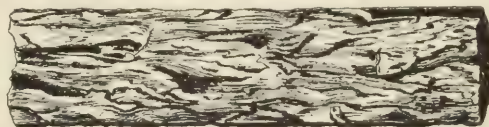
of electricity of suitable amperage to traverse the body of the charge or an appropriate resistor in contact with the charge, but not necessarily in a direction transverse to the direction of movement of the charge.

Roasting Ores and Recovering Zinc. C. J. Reed, Aug. 5, 1913. U. S. Pat. 1,069,178. Zinc sulfid ore is mixed with a

previously oxidized portion of the same material and heated in an oxidizing atmosphere. The soluble zinc compounds are dissolved and the zinc recovered from the solution.

Electrolytically Refining Copper. G. D. Van Arsdale, Aug. 5, 1913. U. S. Pat. 1,069,305. Metallic copper is dissolved from an anode thereof in an electrolyte containing soluble cuprous sulfite and deposited upon a cathode.

Steel Process. J. Churchward, Aug. 5, 1913. U. S. Pat. 1,069,387. This process is based upon the idea that carbon has an astringent effect upon steel, tending to make the particles or fibers of the metal assume a globular form, in consequence of which certain valuable characteristics of the steel are diminished.



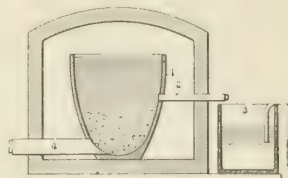
and that this astringent capacity of carbon may be removed by maintaining it at 3100° F. for a certain time. Steel subjected to this temperature for from twenty-five to forty minutes is stated to have a compact, integral, fibrous structure resembling that of wood.

Treating Sulfid Ores. Titus and Barescheer, Aug. 5, 1913. U. S. Pat. 1,069,498. Sulfid ores of metals whose chlorids are readily fusible such as zinc sulfid, are mixed with sodium chlorid, heated and exposed to the action of chlorin.

Manufacture of India-Rubber Goods. W. E. Windsor-Richards, Aug. 5, 1913. U. S. Pat. 1,069,508. Cellulose is mixed with india-rubber at a temperature of about 200° C. and the mixture vulcanized.

Separating Barytes from Ores. C. J. Greenstreet, Aug. 5, 1913. U. S. Pat. 1,069,545.

Barytes is separated from zinc and barytes ores by mixing sodium chlorid therewith and heating in a crucible to a sufficient heat to melt the sodium chlorid. The melted sodium chlorid dissolves the barytes and rises to the top of the crucible from which it may be drawn off. The sodium chlorid is then dissolved in water and drawn off from the insoluble barytes.



Making Artificial Stone. C. A. P. Turner, Aug. 12, 1913. U. S. Pat. 1,069,832. The artificial stone is cast in a mold of sand previously treated with a solution of salt, a soap solution having been applied to the surface of the mold.

Treatment of Iron or Steel for Preventing Oxidation or Rusting. F. R. G. Richards, Aug. 12, 1913. U. S. Pat. 1,069,903. A rust-preventing deposit of manganese and iron phosphate is formed by subjecting the iron or steel to the action of manganese dioxide and phosphoric acid.

Therapeutic Compound and Process of Making the same. E. Hug, Aug. 12, 1913. U. S. Pat. 1,069,951. Erythrene is heated under pressure until a caoutchouc-like substance is produced.

Process of Obtaining Thorium. M. Koss, Aug. 12, 1913. U. S. Pat. 1,069,959. Thorium is obtained by acting upon monazite with sulfuric acid and treating the product with hypophosphoric acid.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF SEPTEMBER, 1913

ORGANIC CHEMICALS

Acetanilid	Lb.	21	@	23
Acetic Acid (8 per cent)	C	2	@	15
Acetone (drums)	Lb.	153	@	16 3/4
Alcohol, denatured (180 proof)	Gal.	36	@	39
Alcohol, gram (188 proof)	Gal.	2	@	2.50
Alcohol, wood (95 per cent)	Gal.	45	@	47
Amyl Acetate	Gal.	2	@	2.30
Aniline Oil	Lb.	101 1/4	@	104 1/8
Benzoic Acid	Lb.	23	@	27
Benzol (90 per cent)	Gal.	21	@	23
Camphor (refined in bulk)	Lb.	42 1/2	@	44
Carbolic Acid (drums)	Lb.	9	@	11 1/4
Carbon Bisulfide	Lb.	6 1/2	@	8
Carbon Tetrachloride (drums)	Lb.	7 1/4	@	8 1/4
Chloroform	Lb.	25	@	35
Citric Acid (domestic), crystals	Lb.	52	@	52 1/2
Dextrine (corn)	C.	3	@	4.00
Dextrose (imported potato)	Lb.	6	@	7
Ether (U. S. P., 1900)	Lb.	14	@	20
Formaldehyde	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite)	Lb.	191	@	20
Oxalic Acid	Lb.	77 1/2	@	8
Pyrogallie Acid (bulk)	Lb.	1	@	1.40
Salicylic Acid	Lb.	28	@	30
Starch (cassava)	Lb.	3 1/4	@	4
Starch (corn)	C.	2	@	3.00
Starch (potato)	Lb.	4 1/2	@	5
Starch (rice)	Lb.	8	@	9
Starch (sago)	Lb.	2 1/4	@	2 1/4
Starch (wheat)	Lb.	5 1/4	@	6 1/2
Tannic Acid (commercial)	Lb.	35	@	36
Tartaric Acid, crystals	Lb.	30 1/4	@	31 3/4

INORGANIC CHEMICALS

Acetate of Lead (brown, broken)	Lb.	7 1/2	@	8
Acetate of Lime (gray)	C.	2	@	2.60
Alum (lump)	C.	1	@	2.00
Aluminum Sulfate (high-grade)	C.	1	@	1.75
Ammonium Carbonate, domestic	Lb.	8	@	8 1/2
Ammonium Chloride, gray	Lb.	57 1/4	@	6 1/8
Aqua Ammonia (drums) 16°	Lb.	21 1/4	@	2 1/2
Arsenic, white	Lb.	3	@	3.50
Barium Chloride	C.	1	@	1.80
Barium Nitrate	Lb.	5 1/4	@	5 1/2
Barytes (prime white, foreign)	Ton	19	@	23.50
Bleaching Powder (35 per cent)	C.	1	@	1.30
Blue Vitriol	Lb.	5 1/8	@	5 1/2
Borax, crystals (bags)	Lb.	3 1/2	@	4 1/4
Boric Acid, crystals (powd.)	Lb.	7	@	7 1/2
Brimstone (crude, domestic)	Ton	22	@	22.50
Bromine, bulk	Lb.	30	@	35
Calcium Chloride, fused	C.	85	@	1.10
Chalk (light precipitated)	Lb.	4	@	4 1/2
China Clay (imported)	Ton	nominal		
Feldspar	Ton	8	@	12.00
Fuller's Earth, powdered, Foreign	Ton	16	@	17.00
Green Vitriol (bulk)	C.	53	@	60
Hydrochloric Acid (18°)	C.	1	@	1.55
Iodine (resublimed)	Lb.	3	@	3.60
Lead Nitrate	Lb.	8 1/8	@	8 1/8
Litharge (American)	Lb.	6 1/4	@	7
Lithium Carbonate	Lb.	63	@	70
Magnesia (powdered)	Lb.	5 1/2	@	6
Magnesite (raw)	Ton	30	@	35.00
Nitric Acid, 36°	Lb.	37 1/3	@	41 1/4
Phosphoric Acid (sp. gr. 1.75)	Lb.	21 1/2	@	25 1/2
Phosphorus	Lb.	45	@	1.00
Plaster of Paris	Bbl.	1	@	1.70
Potassium Bichromate, 50°	Lb.	6 1/4	@	7
Potassium Bromide	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%	C.	3	@	3.65
Potassium Chlorate, crystals	Lb.	8 1/4	@	9 1/2
Potassium Cyanide (bulk), 98-99%	Lb.	19	@	24
Potassium Hydroxide	C.	4	@	5.25
Potassium Iodide (bulk)	Lb.	2	@	3.00
Potassium Nitrate (crude)	Lb.	4 1/4	@	5
Potassium Permanganate (bulk)	Lb.	9 1/4	@	10
Quicksilver, Flask (75 lbs.)	40	@		
Red Lead (American)	Lb.	7	@	7 1/8
Salt Cake (glass-makers')	C.	55	@	65

Silver Nitrate	Oz.	38	@	40
Snapstone in bags	Ton	10	@	12.00
Soda Ash (48 per cent)	C.	55	@	65
Sodium Acetate	Lb.	4	@	4 1/2
Sodium Bicarbonate (domestic)	C.	1	@	1.10
Sodium Bicarbonate (English)	Lb.	2 1/4	@	3
Sodium Bichromate	Lb.	4 1/2	@	5
Sodium Carbonate (dry)	C.	60	@	80
Sodium Chlorate	Lb.	8 1/4	@	9 1/2
Sodium Hydroxide, 60 per cent	C.	1	@	1.52 1/2
Sodium Hyposulfite	C.	1	@	1.60
Sodium Nitrate, 95 per cent, spot	C.	2	@	2.45
Sodium Silicate (liquid)	C.	65	@	1.50
Strontium Nitrate	Lb.	6 7/8	@	7 1/8
Sulfur, Flowers (sublimed)	C.	2	@	2.60
Sulfur, Roll	C.	1	@	2.15
Sulfuric Acid, 60° B.	C.	85	@	1.00
Talc (American)	Ton	15	@	20.00
Terra Alba (American), No. 1	C.	75	@	80
Tin Bichloride (50°)	Lb.	11 1/4	@	12
Tin Oxide	Lb.	46	@	48
White Lead (American, dry)	Lb.	5 1/4	@	6
Zinc Carbonate	Lb.	9	@	10
Zinc Chloride (granulated)	Lb.	4 1/2	@	5
Zinc Oxide (American process)	Lb.	5 1/8	@	6 1/8
Zinc Sulfate	Lb.	2 1/2	@	3

OILS, WAXES, ETC.

Beeswax (pure white)	Lb.	42	@	45
Black Mineral Oil, 29 gravity	Gal.	13 1/2	@	14
Castor Oil (No. 3)	Lb.	87 1/8	@	10
Ceresin (yellow)	Lb.	12	@	22
Corn Oil	C.	6	@	6.70
Cottonseed Oil (crude), f. o. b. mill	Gal.	43	@	43 1/2
Cottonseed Oil (p. s. y.)	Lb.	7 1/2	@	8
Cylinder Oil (light, filtered)	Gal.	21 1/2	@	32
Japan Wax	Lb.	9	@	9 1/2
Lard Oil (prime winter)	Gal.	95	@	97
Linseed Oil (double-boiled)	Gal.	50	@	51
Menhaden Oil (crude)	Gal.	31	@	35
Neatsfoot Oil (20°)	Gal.	98	@	1.10
Paraffine (crude, 120 & 122 m. p.)	Lb.	3 1/2	@	3 1/4
Paraffine Oil (high viscosity)	Gal.	26	@	28
Rosin ("F" grade)	Bbl.	4	@	4.35
Rosin Oil (first run)	Gal.	27	@	31
Shellac, T. N.	Lb.	23 1/2	@	24
Spermaceti (cake)	Lb.	30	@	35
Sperm Oil (bleached winter), 38°	Gal.	72	@	74
Spindle Oil, No. 200	Gal.	18	@	19
Stearic Acid (double-pressed)	Lb.	8 1/2	@	10 1/2
Tallow (acidless)	Gal.	63	@	65
Tar Oil (distilled)	Gal.	30	@	31
Turpentine (spirits of)	Gal.	42	@	42 1/2

METALS

Aluminum (No. 1 ingots)	Lb.	22 1/2	@	23
Antimony (Hallet's)	Lb.	7 1/4	@	8 1/2
Bismuth (New York)	Lb.	2	@	2.10
Bronze powder	Lb.	50	@	3.00
Copper (electrolytic)	Lb.	16 1/2	@	—
Copper (lake)	Lb.	16 1/8	@	—
Lead, N. Y.	Lb.	4	@	—
Nickel	Lb.	50	@	55
Platinum (refined)	Oz.	43	@	44.50
Silver	Oz.	61	@	62
Tin	C.	42	@	43.00
Zinc	C.	5	@	5.90

FERTILIZER MATERIALS

Ammonium Sulfate	C.	3	@	3.10
Blood, dried	Unit	2	@	—
Bone, 4 1/2 and 50, ground, raw	Ton	27	@	28.00
Calcium Nitrate (Norwegian)	C.	2	@	2.10
Castor meal	Unit	3	@	3.10
Fish Scrap, domestic, dried	Unit	3	@	10
Mowrah meal	Ton	nominal		
Phosphate, acid, 16 per cent bulk	Ton	—	@	6.75
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	3	@	3.25
Tennessee, 70-80 per cent	Ton	5	@	5.50
Potassium, "muriate," basis 80 per cent	Ton	38	@	—
Pyrites, furnace size, imported	Unit	0	@	0.13 1/8
Tankage, high-grade	Unit	2	@	2.75 & 10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

NOVEMBER, 1913

No. 11

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly.

Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

The Mining Congress.....	882
Ozone.....	882
Bureau of Mines Coal Analyses.....	883

ORIGINAL PAPERS:

Copper Covered or Copper Clad Steel. By James Otis Handy.....	884
The Condensation of Gasoline from Natural Gas. By George A. Burrell and Frank M. Seibert.....	895
Some Tests of Paints for Steel, Subjected to Alternate Exposure to Air and Fresh Water. By Percy H. Walker and S. S. Voorhees.....	899
The Corrosion of Metals by Water. By A. T. Stuart.....	905
Some Experiments on the Conversion of Long-Leaf Pine to Paper Pulp by the Soda and Sulfate Processes. By Sidney D. Wells.....	906
Investigations with the U. S. Bureau of Mines Modification of the Abel-Pensky and Pensky-Martens Flash-Point Testers. By Irving C. Allen and A. S. Crossfield.....	908
The Titration of Calcium and Magnesium in the Same Solution. By Paul J. Fox.....	910
Comparison of the Kjeldahl-Gunning-Arnold Method with the Official Kjeldahl and Official Gunning Methods of Determining Nitrogen. By T. C. Trescott.....	914
Ortho-Tolidine as a Reagent for the Colorimetric Estimation of Small Quantities of Free Chlorine. By J. W. Ellms and S. J. Hauser.....	915
The Quantitative Estimation of Gliadin in Flour and Gluten. By Geo. A. Olson.....	917
Quality of the Massachusetts Milk Supply as Shown by the Inspection of the State Board of Health. By Herman C. Lythgoe.....	922
The Detection of Gelatin in Sour Cream. By Armin Seidenberg.....	927
A Study of the Composition of Cider Vinegars Made by the Generator Process. By L. M. Tolman and E. H. Goodnow.....	928
On the Decrease of Available Phosphoric Acid in Mixed Fertilizers Containing Acid Phosphate and Calcium Cyanamid. By R. N. Brackett.....	933

LABORATORY AND PLANT:

The Design of an Experimental Wood Distillation Plant. By H. K. Benson and Marc Darrin.....	935
An Apparatus for Determining the Melting Points of Substances of Indefinite Melting Point. By A. P. Bjerregaard.....	938
A Modified Bank of Ammonia Stills. By Fred Berry and L. H. Van Buskirk.....	941

ADDRESSES:

Our Radium Resources. By Charles L. Parsons.....	943
The Relation of Big Business to Industrial Prosperity with Special Reference to Mining. By Charles R. Van Hise.....	946
Fertilizer Chemistry—A Report of Progress. By Paul Rudnick.....	948
Food Standards and their Effect upon Food Law Enforcement. By Floyd W. Robison.....	949

CURRENT INDUSTRIAL NEWS:

An Automatic Chemical Feeder.....	950
Micarta and Bakelite Micarta.....	950
New Centrifugal Pump.....	951
Testing the Liquor in Sulfite Cooks.....	951
The Present Status of the Glass Bottle and Hollow Ware Industries in the United States.....	951
A Sanitary Drinking Fountain.....	954
The Scoria Briquetting Process.....	954
Exposure Tests of Copper, Commercial Aluminum and Duralumin.....	955
Electrolytic Coating of Iron and Steel with Lead.....	955
Tannic Acid from Spent Sulfite Liquor.....	955
A New Desulfurizing Method.....	955

SCIENTIFIC SOCIETIES:

American Chemical Society—Forty-eighth Meeting, Rochester, September 8–12, 1913.....	956
American Chemical Journal to be Combined with the Journal of the American Chemical Society.....	958
American Petroleum Society.....	958
Obituary: Julius Lewkowitsch.....	959

NOTES AND CORRESPONDENCE:

On the Influence of the Ratio of Lime to Magnesia on Plants.....	959
Note on Determination of Fat in Ice Cream.....	960
Design of Surface Combustion Appliances—Correction.....	960
Note on Quantitative Determination of Rosin in Paper.....	960
Platinum Production Increases.....	960

BOOK REVIEWS:

Electro-Plating and Analysis of Solutions; General Index to the Chemical News; Calcium Cyanamid; The American Fertilizer Handbook.....	961
--	-----

NEW PUBLICATIONS.....	962
-----------------------	-----

RECENT INVENTIONS.....	963
------------------------	-----

MARKET REPORT.....	964
--------------------	-----

EDITORIALS

THE MINING CONGRESS

Two notable addresses presented at the recent meeting of the American Mining Congress at Philadelphia are published in this issue of *THIS JOURNAL*.

An address on "Our Radium Resources," by Charles L. Parsons, of the Bureau of Mines, brings out many valuable facts in connection with this most interesting development. He again calls attention to the American carnotite deposits as a new source of radium and the possibility of the production of this material in America. His address includes a discussion of the methods for the extraction of radium, its present market value, and a warning to the medical profession and the public against the activity of impostors. He calls attention to the fact that the United States Bureau of Standards is preparing radium standards by means of which it will be possible for physicians to protect themselves against frauds.

Dr. Parsons announces a new policy in the administration of the Bureau of Mines which is of far-reaching importance in industrial developments of great public interest in the following statement: "I am authorized by the Director of the Bureau of Mines to announce that a cooperative agreement has been entered into with the newly organized National Radium Institute whereby the Bureau obtains the opportunity of scientific and technological study of the mining and concentrating of carnotite ores and of the most efficient methods of obtaining radium, uranium and vanadium therefrom with a view to increased efficiency of production and the prevention of waste." The cooperation of the government in the solution of the radium problem will meet the hearty approval of the medical profession and the general public who are so intimately concerned in the eradication of cancer.

It is also proposed to carry on investigations regarding the physical characteristics of the radium rays in the hope that some or all of the results may be duplicated by physical means.

Reference is made to the forthcoming announcement of remarkable cures effected by the use of radium and meso-thorium, and in view of the sensational announcements in the public press, authoritative statements in this field will be awaited with breathless interest.

The address by President Van Hise, a full abstract of which is published in this issue, will be read with keen interest by those concerned in the problem of scientific conservation. A careful analysis of these problems has led President Van Hise to point out in the most forcible language the obligations of the government and the public in furthering the interests of legitimate conservation, and the address will be exceedingly suggestive reading not only to the people immediately connected with industrial development, but also to those responsible for our legislative and administrative policies.

It is our belief that this address will serve to empha-

size the need of a cooperative policy and legislation calculated to develop conservation instead of the obstructive policy now in general favor.

OZONE

A striking example of the danger of commercializing a popular notion without first subjecting it to proper tests is brought out in two articles in the *Journal of the American Medical Association* for Sept. 27, on the Purification of Air with Ozone. We were taught in our "Prep" school chemistry that it was the "ozone of the country air" which was responsible for the health and longevity of the rural population; and of course the healthful effect of ozone we inferred was due to its value as a disinfectant. Furthermore, ozone is an energetic oxidizing agent; so is hydrogen peroxide; hydrogen peroxide is a valuable germicide; so, we thought, was ozone.

Ohlmüller's experiments, twenty years ago, together with those of several investigators since, discrediting its germicidal action, did not shake the popular faith in ozone. Public officials have readily accepted claims such as the following: (1) Ozone is a necessity for the destruction of infectious germs, for the sterilization of air in operating rooms, for the purification of air in homes of persons suffering from contagious diseases, and for giving to offices and homes the invigorating air of country, seashore and mountain. (2) Ozone cannot exist except momentarily in air containing organic matter, and therefore the presence of ozone is an indication that the air is sterile and devoid of organic matter. (3) Ozone is unique as a germicide by reason of the fact that it has no deleterious effect on the higher forms of animal life, owing to the low percentage of carbon in their structure.

In the first of the two articles mentioned, "Ozone: Its Bactericidal, Physiologic and Deodorizing Action," by E. O. Jordan, M.D., and A. J. Carlson, M.D., of Chicago, the authors describe an extensive series of experiments undertaken by them at the suggestion of, and under a grant from *The Journal of the American Medical Association*. Their investigation was complete and exhaustive and their data fully justify their conclusions and summary which we quote:

"So far as the destruction of bacteria is concerned, ozone has little or no value. Some bacteria are undoubtedly killed by ozone, especially if they are in a moist condition and are in contact for several hours with a current of ozone coming direct from the generator. In practice, however, the fact is of slight importance. Human beings are injuriously affected by amounts of ozone far less than are necessary to produce even this slight bactericidal effect, and there is no evidence for supposing that a quantity of ozone that can be tolerated by man has the least germicidal action. If disinfection of a closed room without inmates is desired, this can be much more effectively carried out by the use of formaldehyde or some other familiar gaseous disinfectant than by ozone. Ozone has no place in practical room disinfection.

"Ozone is not an actual 'deodorizer' in concentrations that can obtain in practical ventilation. In very great concentra-

tions ozone seems capable of oxidizing some odorous substances so that the odors are diminished or changed, but the change may be in the direction of increasing the disagreeableness of the odor. In very great concentrations ozone 'masks' most odors by its own intensive odor, and possibly by fatigue or anaesthesia of the olfactory epithelium. Certain odors are masked by ozone even in weak concentrations. Is such masking of odors desirable and generally advantageous? We think not. It is probable that the injury to the respiratory tract by ozone in sufficient concentration to act as an effective mask is of greater moment than the deleterious action of most odors. Except in special industrial processes, the unpleasant odor of the inspired air in shops, offices or living rooms is usually a sign that the air needs to be renewed or changed. Why should we put out of commission the sense organ which aids us in determining whether or not the air is fit to breathe? It seems to us that this is wrong in principle, and that ozone is being used and will be used as a crutch to bolster up poor ventilating systems. Ozone does not make 'pure air' any more than strong spices make pure food.

"In concentrations that appreciably affect man and animals, ozone appears to have uniformly an injurious action. This injurious action is primarily on the respiratory passages—irritation of the sensory nerve endings, and irritation, corrosion and depression of the epithelial cells. The depression of the alveolar epithelium leads to changes in the gaseous exchange in the lungs, and secondarily to changes in the blood, and ozone headache, depression and drowsiness are produced.

"Hill and Flack [*Proc. Roy. Soc.*, 82, 404 (1911); *Jour. Roy. Soc. Arts.*, 60, 344 (1912)] point out that ozone gives a certain 'tang' to the air, and thus relieves the impurity (temperature and moisture) which is apt to obtain in offices and assembly rooms. This tang is a combined effect of ozone odor and the ozone irritation of the sensory nerves in the respiratory tract. We have seen that this acts (reflexly) on the vascular mechanism and it may temporarily 'whip up' a fagged brain. But is this ozone tang any more beneficial or any more physiologic than a whiff of smelling-salts or a puff of the cigarette? We recognize that a certain amount of variation in the rate of movement and in the temperature of the air about us aids in maintaining the tonus of the brain, but our ventilation engineers must reproduce the variability of outdoors by actual variations in the air and in the rate of movement of the air in the ventilating systems, and not by adding a poisonous gas to the air. Nor can we accept the suggestion of Hill and Flack that small amounts of ozone may be of therapeutic value in certain diseases of the respiratory tract by reason of the hyperemia following the ozone irritation. The cells injured by ozone are probably more readily invaded by bacteria, and have less than normal power of growth and healing despite the hyperemia. And all bacteria so far studied are much more resistant to ozone than are the cells of the respiratory tract of man and experimental animals. The physiology of ozone points to the conclusion that the use of this poisonous gas as a therapeutic agent is either valueless or injurious."

The second article, "The Alleged Purification of Air by the Ozone Machine," by W. A. Sawyer, M.D., Director of the Hygienic Laboratory of the California State Board of Health, and his co-workers, Beckwith and Skolfield, though not as extensive, is no less convincing than the first. The conclusions of these authors are quoted also:

"The gaseous products of the two well-known ozone machines examined are irritating to the respiratory tract and, in considerable concentration, they will produce edema of the lungs and death in guinea pigs.

"A concentration of the gaseous products sufficiently high to kill typhoid bacilli, staphylococci and streptococci, dried on

glass rods, in the course of several hours, will kill guinea pigs in a shorter time. Therefore these products have no value as bactericides in breathable air.

"Because the products of the ozone machines are irritating to the mucous membranes and are probably injurious in other ways, the machines should not be allowed in schools, offices or other places in which people remain for considerable periods of time.

"The ozone machines produce gases which mask disagreeable odors of moderate strength. In this way the machines can conceal faults in ventilation while not correcting them. Because the ozone machine covers unhygienic conditions in the air and at the same time produces new injurious substances, it cannot properly be classed as a hygienic device."

It is to be hoped that the results of these investigators will receive sufficient publicity to correct popular ideas on the germicidal action of ozone and that the work will not have to be repeated as it has been so many times within the last twenty years.

A. M. BUSWELL

BUREAU OF MINES COAL ANALYSES

Government purchasing agents, designing and operating engineers, and the fuel departments of industrial concerns, dealers in large quantities of coal, and persons interested in the distribution and character of the different coals in the United States will find valuable information in a report just issued by the United States Bureau of Mines as *Bulletin 22*, entitled "Analyses of Coals in the United States, with Descriptions of Mine and Field Samples Collected between July 1, 1904, and June 30, 1910." This report contains the analyses of 5,000 samples of coal taken from 1,500 coal mines and prospects situated in the various coal fields of the United States. Not only all of the important fields are represented, but practically all of the more important mining districts.

The purpose of the Bureau in compiling and publishing this information is to present reliable information regarding the chemical composition and heating value of the coals. The samples of coals were collected by experienced men according to a definite and uniform system, and were analyzed under carefully controlled conditions, so that there might be no question as to the relative merits of the different coals so far as this can be determined by chemical analyses and determinations of heating values.

An increasing proportion of the coal consumed in the power stations and the larger manufacturing plants of the country is now being purchased under specifications based on chemical analyses and calorimetric determinations of heat units. In the purchase of fuels many matters formerly left to chance are now carefully investigated. It is the aim of mechanical engineers to construct furnaces and to arrange the heat-absorbing surface in a furnace with reference to the peculiar character of the fuel which is to be burned. Noting the composition of the fuel and constructing the furnace with reference to it, he can assure efficient and smokeless combustion. Moreover, in any particular market, the choice of coal is limited generally by its quality and by freight rates to one or two fields in which the character of the coal beds is comparatively uniform. Having on hand a representative analysis

of the coal from a given bed in any particular district, the engineer can determine whether the coal he receives comes from the bed and the district stated, and whether it is being prepared for market as carefully as it should be. Wide variations in the compositions and heating values of the coals from different districts and from different beds make comparable analyses almost indispensable to engineers having to install boiler or gas-producer plants in different cities, as well as to railroads and steamboat companies, and to the engineers and purchasing agents of the various departments of the United States Government.

The Bureau of Mines report is in two parts: one gives the methods used in collecting and analyzing the samples and the results of the analyses; the other

gives the exact location from which each sample of coal was taken, together with a description of the characteristic features of the coal bed at the point of sampling, the nominal capacity of the mine and such notes on the preparation of the coal as might be useful to consumers. The data contained in these two volumes are not equalled in scope and detail and in value for comparative purposes by the figures that have been published by any other coal-producing country in the world. The Governments of some of these countries have published analyses of coals from different mines and from different districts but, with few exceptions, the samples of coal were not collected and analyzed under a uniform system that would make the results comparable in all respects.

ORIGINAL PAPERS

COPPER COVERED OR COPPER CLAD STEEL¹

THE MANUFACTURE, PROPERTIES AND USES OF COMPOSITE METAL MADE BY ALLOYING OR WELDING COPPER AND STEEL

By JAMES OTIS HANDY

Of the metals in common use, copper is the only one which occurs naturally in large quantities in the metallic state. The great native copper deposits of Michigan are the best illustration which could be found of the extraordinary resistance of copper to corrosion.

The metals zinc, tin, and lead, which are commonly used as protective coatings for iron and steel, do not occur in the native state and do not approach copper in durability under atmospheric conditions. Their use is comparatively modern and in the case of tin (now selling at 41 cents per pound) is commercially possible only because of the exceedingly thin coat which may be put on (2 lbs. per box means a 0.00012 inch tin coating).

The necessity of protecting iron from corrosion and the desirability of strengthening copper alloys used for primitive tools and weapons led, at a very early period, to the use of a combination of an iron core and a bronze covering. Such articles have been found in the ruins of Nimroud, an ancient Assyrian city, and among the remains of the Swiss Lake Dwellers (Friend: "Corrosion of Iron and Steel," page 8).

For similar reasons, the union of iron or steel with copper in such a manner as to obtain a composite metal retaining unimpaired the good qualities of both metals has long been a desideratum.

Many inventors have given their attention to the difficult problem of securely uniting iron or steel with copper, and the patent literature of the United States and of European countries contains many illustrations, chiefly of unworkable or imperfect processes.

The earliest patent we have found was one issued to Poole, of England, in the year 1821. Copper or brass was melted in a shallow cast iron pan (British Patent 4598 of 1821).

¹ Paper presented at the 48th meeting of the American Chemical Society, Rochester, September 8-12, 1913.

The commercial electro-deposition or electroplating of copper on iron or steel seems to have started before 1840, in England. This process has been used chiefly for the production of thin coatings, but processes have been developed by Elmore and others for making, by electro-deposition, copper tubes of considerable thickness.

Such a process was undoubtedly used commercially by the manufacturers who, in the year 1883, supplied to the Postal Telegraph Cable Company bimetallic wire consisting of a hard steel core wire 0.120 inch in diameter surrounded by a seamless, electro-plated, closely-fitting copper tube having approximately 0.042 inch walls. The ratio of steel to copper by weight was about 1 : 3 (Figs. 1 and 2).

The same company used also a compound wire consisting of a steel core wire surrounded first by a thin electro-deposited copper sheath 0.008 inch thick and then by a wrapping of heavier copper with walls 0.044 inch thick (Figs. 3 and 4).

In neither type of wire was there a bond between copper and steel other than a close conformation. The workmanship was so excellent, however, that samples taken down after 28 years' exposure in the line from New York to Chicago showed absolutely no corrosion of the steel core. The copper sheaths retained the dimensions given above.

Desire to solve the problem of uniting copper with iron or steel would naturally lead to attempts to make a weld by processes analogous to the one successful with iron or mild steel. When, however, heating and hammering iron and copper together failed, even with the use of various fluxes, to produce a weld, it became apparent that the problem was a difficult one.

Inventors tried to follow established methods for coating one metal with a more fusible one, *e. g.*, the coating of iron or steel with zinc, tin, or tin-lead alloy by passing the former metals, properly cleaned, through baths of the melted, fusible metals. The high melting point of copper and its strong tendency to oxidize when melted, offered great obstacles. Coatings made by dipping steel into melted copper are always thin if the steel is hot, and are usually imperfectly adherent.

The ideas of casting melted copper in considerable amount against an iron or steel base or around a steel core, or of casting iron or steel inside a copper tube, were conceived and tried by the following inventors:

"Rollers for Printing Fabrics," British Pat. 1924 of 1856; Tytherleigh. *Method*.—Dipping iron in melted copper; then heating and casting more copper around it.

"Improvement in Coating Metals," U. S. Pat. 21,797 of 1858; Hiler. *Method*.—Casting iron or steel in a copper mold and completing the union by rolling.

Specification.—"I have discovered that the best union of the iron or steel with its coating metal can be made by heating the iron or steel until it is fused and bringing it while in that condition in contact with the coating metal, and keeping it so in con-

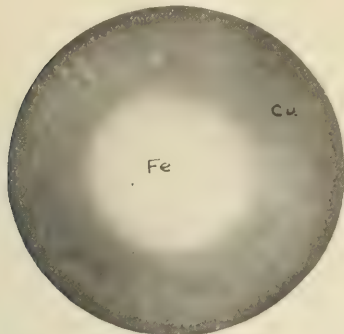


FIG. 1 X 11

"Postal Telegraph" Wire with Steel Core and Entirely Electrodeposited Copper Covering

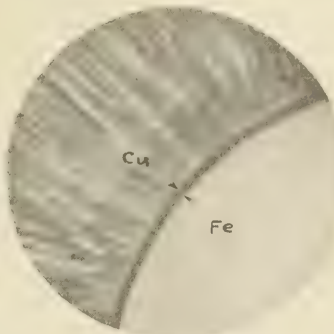


FIG. 2 X 44

"Postal Telegraph" Wire with Steel Core and Entirely Electrodeposited Copper Covering

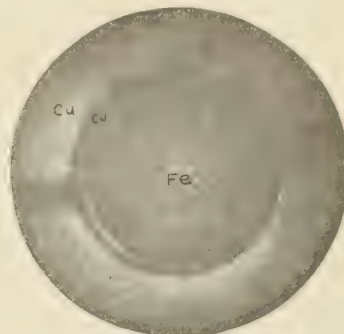


FIG. 3 X 11

"Postal Telegraph" Wire with Steel Core, Electrodeposited Tube, and Folded—on Copper Cover

Specification.—"In carrying my invention into effect, I take a hollow iron cylinder, of somewhat less diameter than the roller or cylinder to be manufactured. I prefer to perforate the said cylinder with holes. I clean the said iron cylinder by acids or otherwise. I afterwards cover the said iron cylinder with borax or other suitable flux, and heat it sufficiently to fuse the flux thereon. In another furnace I heat a pan or vessel (made of a material capable of bearing the requisite heat), the said pan or vessel containing copper, brass, or other alloy of copper. When the copper or alloy is fused, I put the iron cylinder therein and turn it, so as to coat it with the metal. I take the cylinder from the said pan or vessel, and while hot I put it in a hollow cylinder or mould, closed at bottom with clay or other suitable

tact until both metals have become cooled to a proper temperature."....."On the melted iron being poured into the mold in contact with the coating metal the latter becomes fused by the heat of the former; but before it is so fused the iron has parted with so much of its heat as to be sufficiently chilled to prevent the coating metal from mixing with the iron, and also to prevent the said coating metal from sinking down and occupying the bottom of the mold."

Claim.—"What I claim as my invention, and desire to secure by Letters Patent, is: The coating iron or steel with copper, silver, or brass, or alloys where silver or copper is used, by bringing the iron or steel, while in a melted state, into contact with the coating metal, and allowing them to so remain until the two

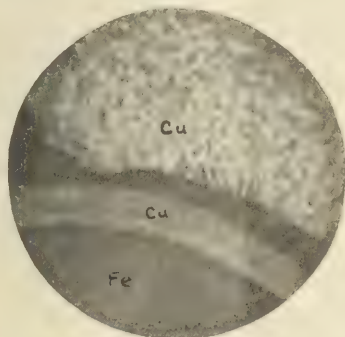


FIG. 4 X 44

"Postal Telegraph" Wire with Steel Core, Electrodeposited Tube, and Folded—on Copper Cover



FIG. 5 X 50

Commercial Alloy Union of Copper and Iron. Longitudinal Section of "Monnot-Duplex" Wire



FIG. 6 X 44

Commercial Alloy Union of Copper and Iron. Cross Section of "Duplex Copper-Clad" Wire

material. I place a core or axis in the iron cylinder, and adjust it, by screws or otherwise, in the axis of the mould. I put the whole into a furnace, and when the coating on the iron cylinder begins to melt I pour fused copper or copper alloy into the mould, and I maintain the heat until the copper or alloy is thoroughly incorporated with the coating on the iron cylinder; the fire is then slackened, and the whole allowed to cool. The roller or cylinder is afterwards finished by the process of turning."

metals have become hard by cooling, substantially as specified."

Suggested Uses of Hiler Product.—Stair rods, trunk nails and bands, buttons, etc.

"Improvement in Line-Wires for Telegraph," U. S. Pat. 47,940 of 1865; Farmer and Milliken. *Method*.—Casting copper around an iron bar; then rolling and drawing into wire. This seems to be the pioneer patent on telegraph wire composed of copper with a steel core.

Specification.—"In the construction of aerial telegraph lines the general practice, as is well known, is to use iron wire for transmission of the electric current, this wire being galvanized or coated with a thin coating of zinc to prevent oxidation. In the earlier constructions of lines it was sometimes attempted to use copper wire, but for want of tensile strength in such wire its use had to be abandoned. Yet the employment of copper wire is a desideratum on account of its great superiority over iron as a conductor, and could its tensile strength be made equal to that of iron it would, to a great extent, supersede the iron wire."

"Our invention, therefore, consists in a copper telegraph wire cored or covered, for the purpose of strength, with iron or steel."

"In carrying out the invention or constructing this compound wire we prefer to core the copper with iron, first casting the copper around an iron bar and then by the processes of rolling and drawing attenuating the same into wire by the well-known methods of wire-drawing. It will be obvious, however, that the iron can be placed around the copper and the resultant bar drawn out into a wire, leaving the copper in the center; but the first-named construction we consider preferable, as the iron is protected from oxidation, and the manufacture of this wire is the more practicable."

Claim.—"As a new article of manufacture, a telegraph wire reinforced, for the purpose of strength, with a core or cover of iron or steel, the wire being made by drawing a compound bar of the two metals."

"Improvement in Combining Copper with Cast Steel," U. S. Pat. 73,375 of 1868; Park. *Method.*—Casting steel in a hollow copper ingot, previously heated.

Specification.—"A combination or union of copper with some harder and stronger metal has been long needed for many purposes in the arts and manufactures, such as locomotive fire-box sheets, wire for ships' rigging, rods, bolts, spikes, and various other articles for which copper alone cannot be employed, owing to its softness and want of strength."

"My invention consists of combining copper with cast steel, by casting the molten steel on or around the copper, which is previously heated, thus forming an ingot which may be hammered, rolled, or otherwise worked into any desired shape, the steel being tempered or hardened as may be desired after it is worked."

"If it is desired to have steel in the center and copper all around it, as is required for making copper-coated steel wire, or copper-coated spikes or rods, I prepare a hollow ingot of copper, into the center or cavity of which, after it has been heated to a good red heat, I teem or pour the molten cast steel. In this case no mould would be necessary, but may be used if preferred. Such ingot may be drawn out into wire, or worked into other articles, such as bolts, spikes, etc."

Claim.—"Combining copper and cast steel by heating the copper to a good red heat, and teeming or pouring thereupon liquid molten cast steel, substantially as and for the purposes hereinbefore described."

"Process of Manufacturing Compound Telegraph Wire," U. S. Pat. 310,995 of 1885; Farmer. *Method.*—Copper plated iron wire drawn through melted copper.

Claim.—"1. The method herein described, of manufacturing compound telegraph wire, which consists in electroplating a steel or iron wire with a thin film of copper, then drawing the same through molten copper and shaping the coating in substantially the manner set forth."

"Improvements in the Manufacture of Wires, French Pat. 168,133 of 1885; Martin. *Method.*—(a) Casting copper in iron tube. (b) Casting copper around medial part of iron bar and then reheating and rolling, etc."

In an 1888 supplement to the above patent he described casting copper around the medial part of a

steel bar. He then rolled and drew it. Martin seems to have introduced bimetallic wire very extensively in France and elsewhere in Europe. His work appears to be the commercial development of the ideas of Farmer and Milliken.

Claim.—"I claim in this supplement to my principal patent my perfected method of making bimetallic wires in which the metal which forms the exterior envelope is more ductile than that which forms the interior core, this method consisting essentially in casting the metal intended to form the envelope around the medial portion of the rod which must form the heart of the wire, and in extending the rod so partially covered by the metal of the envelope by alternate passes first in one direction and then in the other between the rolls of a rolling mill."

"Process of Producing Compound Metal Bodies," U. S. Pat. 853,716 of 1907; and "Copper Clad Iron and Steel," 893,932 of 1908; Monnot.

Monnot develops further the plan suggested by Tytherleigh, Farmer and Milliken, and Martin. He uses supermolten, *i. e.*, very hot melted copper to give a thin initial coating and then casts copper around the coated steel billet. He finally reheats and rolls.

Specification.—(U. S. Pat. 853,716.) "When at the supermolten temperature many metals are very sensitive to flame, gases and other bodies, readily becoming impure; and there is reason to believe that at such temperatures such metals have a solvent action on other solid metals placed in them."

"By applying only a thin film coating by the action of supermolten metal, and then applying the main coating by means of metal nearer its point of solidification, there is less probability of reduction of quality of the coating metal. However, the main coating may be and frequently is formed entirely from supermolten metal, this method having the important advantages of requiring less manipulation and fewer baths of molten metal."

Claims.—(U. S. Pat. 893,932.) "1st. As a new article of manufacture, a ferrous metal base, having a welded-on, continuous, poreless, dense coating of copper united thereto by a union resisting temperature changes, cutting tools, and mechanical stresses, said coating having the properties of metal set from a liquid state."

"2nd. As a new article of manufacture, an extended metal article comprising a ferrous metal base and a continuous, poreless, dense coating of copper weld-united thereto, by a union resisting temperature changes, cutting tools, and mechanical stresses; said ferrous base and copper coating having been extended together."

In all of the above processes except those of Tytherleigh and Monnot, heating and rolling are essential to complete the union between the two metals. The unions are more or less perfect according to whether the operator reads into the patents effective means of keeping the abutting surfaces clean at the critical instant. The products of most of these processes contain copper and iron alloys because steel dissolves readily in melted copper and melted steel dissolves copper with great speed. Copper in steel or iron in copper are disadvantageous electrically because they harden the principal metal and diminish the conductivity of composite wire. Copper in steel retards its corrosion (Buck, THIS JOURNAL, 5, 447).

It is possible by skilful regulation of temperatures of casting and by proportioning correctly the amounts of melted metal and of the solid metal core or tube, to avoid alloy formation, except in the Tytherleigh, Park, and Monnot procedures. In the latter, an

alloy is intentionally made, and the fact is considered an important mechanical advantage, counterbalancing, in the inventor's opinion, the higher electrical resistance.

There have been a number of attempts to utilize hydraulic pressure and means other than rolling pressure to weld cast copper while still hot to steel. As examples of these are the following:

"New Process of Manufacturing Bimetallic Plates and Wires," Belgian Pat. 171,442 of 1903, *Martin*.

Claim.—"A process of making bimetallic plates and wire, which consists in applying on the inside walls of a conical ingot mold, widened at the bottom, a lining or sheet of copper, of silver, of brass, etc., covering all or a part of the surface of the ingot mold, then running the steel into the mold, and (finally) forcing out the ingot through the small end of the mold by the use of a hydraulic press whose piston presses against the large end of the ingot, in such a way as to weld the two metals and to suppress all flaws between them."

"Process of Making Bimetallic Products," U. S. Pat. 853,932 of 1907, *Monnot and Martin*.

The chief feature of these patents, which both cover the same processes, is the forcing of a cast, composite

of the plates from scale, oxid, or other impurities, then coating or covering one or more faces of this plate with a metal or an alloy thereof having a lower fusing point, then applying to this coated surface a plate of metal or an alloy of the same character as the coating, but free from any coating, then applying heat to the two plates, and finally uniting by pressure, substantially as described."

The new methods introduced by Griffith were the plating of the iron with copper, either by chemical or electrical deposition, and then placing copper and copper-coated iron in close contact, heating them up and rolling them together at the proper temperature. The copper-plating of the iron prevents its oxidation and keeps its surface in condition to unite firmly with the copper when the two metals receive a proper rolling pressure at the right temperature. The temperature recommended by Griffith was about 1700° F. The writer has observed that at 950° C. (1742° F.) welding of copper to copper-plated iron, rolled as composite cylindrical billets, was complete after the first few passes. Welding by rolling pressure is the most effective method. Forcing through a die or otherwise

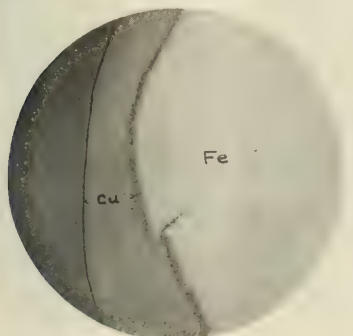


Fig. 7 X 44
Commercial Alloy Union.
Defective Steel
Core

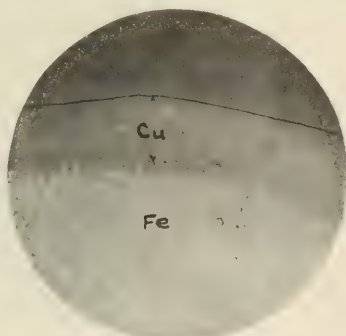


Fig. 8 X 44
Commercial Weld Union of Copper and Iron.
Cross Section of "Standard
C. C. C." Wire

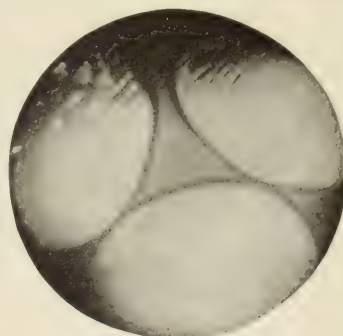


Fig. 11 X 11
Alloy Union of Copper
and Iron at
1130° C.

ingot through a die, or the use of hydraulic pressure on properly heated, flat slabs, in order in both cases to get a weld before further working. This practice, even if successful, seems expensive and is superfluous if heating and rolling are to follow.

In the process of *Griffith* (U. S. Pat. 580,344 of 1897) for "Uniting or Welding Metal," there was a return to the original idea of welding without first melting either copper or iron.

Specification.—"To this end the invention consists in the process hereinafter described, in which the plate, bar or other article of iron or steel is first cleansed from scale or oxid; its surface or surfaces then covered with a coating or deposit of copper or an alloy of copper or any other suitable metal or alloy thereof capable of being deposited by chemical or electrical deposition or otherwise, in this instance by the action of a bath of a solution of the salts of copper; is then placed face to face with a sheet or plate of copper or an alloy thereof; is then heated to the proper degree, and, finally, is passed through rolls or is subjected to pressure requisite to effect the perfect and intimate welding of the metals."

Claim.—"The herein described process of uniting or welding plates of metal of different kinds, which consists in cleansing one

using hydraulic pressure are very cumbersome methods.

German Pat. 152,042 of 1903, *Wachwitz*.

This inventor uses aluminum as intermediary in effecting a union of copper and iron. He rolls clean aluminum and copper sheets together at about 800° F. He rubs metallic aluminum into the surface of clean iron. His first operation in sheet manufacture is to bind the copper-aluminum sheet to the iron-aluminum slab and heat and roll. These complicated operations are said to produce a secure weld.

U. S. Pat. 1,065,727 of 1913, *Rockey and Eldridge*.

This is an attempt to make copper-clad steel by dipping into successive baths of melted copper covered with melted boric anhydride. It is mentioned only to show that efforts are still being made along the lines indicated.

It has been noted that welded composite metal made by the Griffith process contains little or no copper-iron alloy. Spring, in 1878, by pressure alone (without heat), produced alloys of certain mixed metal

filings (Law, "Alloys," page 3). It has also been asserted that solid metals may be united in thin layers at the point of contact by the use of heavy pressure and that the union is an alloy. It might naturally be expected that when forced together at 950° C., copper and iron might superficially alloy. The fact remains, however, that copper-clad steel wire made by the "Colonial" and "Standard" developments of the Griffith process,



FIG. 9—WIRE-DRAWING BENCH

The Dies are at the Left of Each Reel. Each Die and Reel Form an Independent Unit

has a conductivity almost the same as the sum of the conductivities of the iron and copper composing it. This is not true of copper alloyed with iron nor of the products of other processes with which the writer is familiar.

TABLE I—CONDUCTIVITIES BASED ON PERCENTAGES BY VOLUME, CONDUCTIVITY OF COPPER BEING ASSUMED AS 100 AND OF SOFT STEEL AS 13.5

B % steel	Conductivity of the steel	A % copper	Conductivity total	Ratio A : C
0	0	100	100.0	1 : 1
10	1.35	90	91.35	1 : 1.015
20	2.70	80	82.70	1 : 1.034
30	4.05	70	74.05	1 : 1.058
40	5.40	60	65.40	1 : 1.090
50	6.75	50	56.75	1 : 1.135
55	7.43	45	52.43	1 : 1.165
60	8.10	40	48.10	1 : 1.202
65	8.78	35	43.78	1 : 1.251
70	9.45	30	39.45	1 : 1.315
77	10.40	23	33.40	1 : 1.452
80	10.80	20	30.80	1 : 1.540
90	12.15	10	22.15	1 : 2.215
100	13.5	0	13.5

The accompanying tables show how remarkably uniform the "welded" copper-clad wire is and how closely the actual and the calculated conductivities correspond. In the "alloyed" type occasional samples show close agreement, but in general there is a noticeable deficiency and in several cases the *low actual conductivities* are remarkable.

The better showing of the "welded" type is undoubtedly due to the high purity of the copper coating, which is free from iron alloy or oxide of copper.

In this connection it is of interest to endeavor to define "weld" and to compare welded with alloyed copper-clad steel.

A weld, until the advent of electric and oxy-acetylene methods of uniting metals, meant simply the join-

TABLE II—CONDUCTIVITIES BASED ON PERCENTAGES BY WEIGHT, CONDUCTIVITY OF COPPER BEING ASSUMED AS 100 AND OF SOFT STEEL AS 14.3

B % steel	Conductivity of the steel	A % copper	Conductivity total	Ratio A : C
0	0	100	100.0	1 : 1
10	1.43	90	91.43	1 : 1.016
20	2.86	80	82.86	1 : 1.036
30	4.29	70	74.29	1 : 1.060
40	5.72	60	65.72	1 : 1.095
50	7.15	50	57.15	1 : 1.143
55	7.87	45	52.87	1 : 1.175
60	8.58	40	48.58	1 : 1.215
65	9.30	35	44.30	1 : 1.266
70	10.01	30	40.01	1 : 1.333
77	11.00	23	34.00	1 : 1.478
80	11.44	20	31.44	1 : 1.570
90	12.87	10	22.87	1 : 2.287
100	14.3	0	14.3

TABLE III—CONDUCTIVITY OF SOFT STEEL WIRES CONTAINED IN COPPER-CLAD STEEL

		Maximum	Minimum	Average
"Welded" type.....	12 samples	14.41%	14.04%	14.28%
"Alloyed" type.....	9 samples	14.02%	13.44%	13.74%

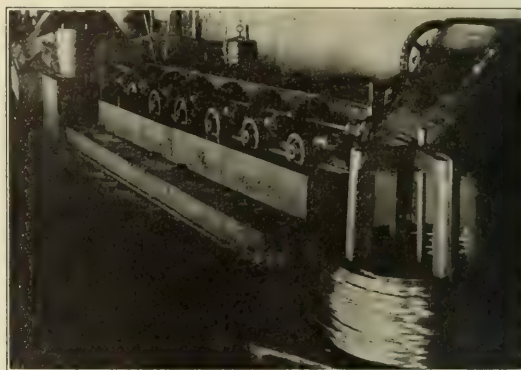


FIG. 10—CONTINUOUS WIRE-DRAWING MACHINE
Six Size Reductions in One Operation

TABLE IV—ACTUAL CONDUCTIVITY OF COPPER-CLAD WIRE SAMPLES COMPARED WITH CALCULATED CONDUCTIVITY

	Copper	Conductivity	
		Actual	Calculated
"Welded" type.....	22.8 %	35.20%	34.60%
"Welded" type.....	24.06	35.80	35.68
"Welded" type.....	20.15	32.24	32.37
"Welded" type.....	23.44	35.25	
"Welded" type.....	23.42	35.45	
"Welded" type.....	23.65	35.11	
"Welded" type.....	23.06	35.43	35.28
"Welded" type.....	23.66	35.13	
"Welded" type.....	24.32	36.12	
"Welded" type.....	23.59	35.42	
"Alloyed" type.....	44.00	34.00	52.57
"Alloyed" type.....	43.50	45.72	52.15
"Alloyed" type.....	34.20	43.80	44.27
"Alloyed" type.....	22.53	33.92	34.38
"Alloyed" type.....	33.65	41.57	43.80
"Alloyed" type.....	41.20	47.42	50.20
"Alloyed" type.....	22.75	33.52	34.57
"Alloyed" type.....	31.90	38.49	42.32
"Alloyed" type.....	38.86	46.81	48.21
"Alloyed" type.....	40.35	48.91	49.48
"Alloyed" type.....	35.20	43.52	45.11
"Alloyed" type.....	35.10	45.47	45.03
"Alloyed" type.....	38.80	45.06	48.16

ing securely by pressure of two pieces of heated, plastic metal. Usually both pieces of metal were of iron

or mild steel, but it has been found that the process may be applied to other metals which pass through a plastic state before fusion. Copper is such a metal and platinum is said to be similar. It is therefore quite proper to speak of unions between plastic copper and plastic iron as welds in the original sense of the term.

Unions made by fusing two metal surfaces together are more analogous to soldered joints than to welds as commonly understood.

Nevertheless, it is held by Prof. Sauveur that there is no "true" weld between dissimilar metals (he considers iron and copper dissimilar) unless there is a "crystalline interlocking" at and across the junction, and this structure is not produced unless one of the metals is in a fused condition and therefore capable of alloying with the other metal. Prof. Sauveur therefore classifies copper-iron alloy welds (Figs. 5, 6 and 7) as true welds, and unions such as he believes the Griffith-Colonial-Standard process gives (Fig. 8), as only adhesions, not really welds.

Be the definition what it may, the union of copper and iron in the Griffith process is so secure that it resists the remarkably severe stripping action to which it is subjected in wire drawing (Figs. 9 and 10). The composite metal extends evenly in rolling and drawing so that 0.004 inch wire (No. 40 B. & S.), hair-like in fineness, still carries practically the original percentage of copper coating. Some variation occurs, as would be expected, even though there is no stripping.

Sample "J. O. H. No. 13" (regular "welded" copper-clad wire) contained at No. 40 gauge (0.004 inch) 21.2 per cent of copper as against 23.06 per cent in the same wire at No. 10 size. It is not believed that this represents loss of copper, but merely slight unevenness in coating. Larger samples would probably correspond more closely. There is, of course, some loss of copper during the manufacturing processes which precede wire drawing.

CONDITIONS UNDER WHICH MELTED COPPER WILL UNITE WITH STEEL

The difficulty in effecting a union between heavy steel objects and melted copper is the chilling effect of the solid mass upon the melted metal. It is doubtless for this reason that Monnot recommends the use of "supermolten" copper (above 2550° F.) and also prescribes heating the steel billet to redness.

When, however, steel and copper are at the same temperature and are clean, they unite instantly, as soon as the copper melts (1085° C., 1987° F.).

The following experiment proves the statement just made:

Several clean steel wire nails were made into a bundle with an equal number of pieces of copper wire disposed symmetrically. The bundle was secured by two bands of copper wire and was dropped into melted borax sufficient to completely cover it. The temperature was gradually raised until the copper melted, when it ran like solder over the surface of the steel nails, cementing them firmly together (Figs. 11 and 12).

The effect of either prolonged contact of melted

copper and solid steel or of higher temperature than 1100° C. in promoting the formation of copper-iron alloy is shown by the following experiment:

Pieces of copper-clad wire of equal length were ex-

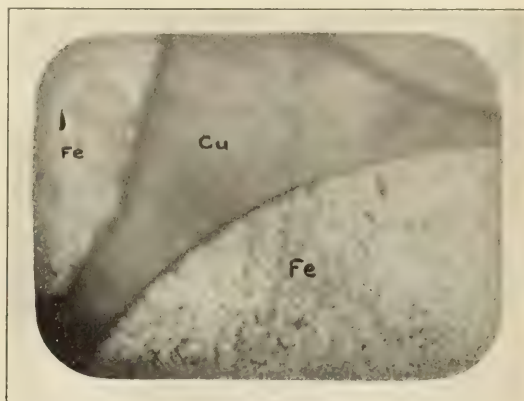


FIG. 12 X 50
Alloy Union of Copper and Iron at 1200° C.

posed, under melted borax, in separate crucibles, to various temperatures. The amounts of steel dissolved by the melted copper globules indicate the vigor with which the action proceeds.

Temperature	Time	Iron in copper button
1200-1250° C.....	5 minutes	3.18%
1300-1320° C.....	3 minutes	4.20
1330-1400° C.....	2 minutes	5.12
1400-1450° C.....	4 minutes	8.53

A second experiment showed that, when left at 1420° C. (2588° F.) for 15 minutes, melted copper dissolved nearly all of an $11/16$ inch steel rod which was vertically immersed in it. The copper finally contained from 8.7 per cent to 14.35 per cent of iron in top and bottom, respectively.

In a third experiment, which was intended to give some light as to the effect of very brief contact of copper and steel at 1420° C., it was found that even when the crucible in which melted copper and iron had been brought together (at 1420° C.) was removed from the furnace in 30 seconds, the copper had alloyed with 2.85 per cent of its weight of iron.

At 1200° C. a parallel experiment gave iron 1.85 per cent in the copper.

These experiments show how quickly iron and melted copper unite when both are at the same temperature. This is a detriment if the product is to be used for electrical purposes. For other uses, where the product cannot be reheated or worked, it is a matter of interest to know just how the metals may be united.

METHODS OF MANUFACTURE

There are two types of copper-clad steel which are manufactured and used: (1) the type which depends on a copper-iron alloy for the bond; and (2) the type which consists of copper welded to steel by proper methods without melting the copper.

(1) The method of manufacture of the first type of

copper-clad steel is described by Tassin.¹ It consists essentially in preparing round steel billets approximately 5 inches in diameter and 20 inches long, which are cleaned by pickling and then heated up in molds which serve the double purpose of excluding the air at first and finally of receiving the annular copper jacket which is cast around the steel core. Producer gas is run through the mold to hinder oxidation of the steel and copper. The heated billet and mold are lowered into a bath of what is called by Monnot, the inventor, "super-molten copper" having a temperature approximating 2550° F., for the purpose of forming a film of copper-iron alloy on the surface of the steel billet. For this purpose the mold is opened after it enters the copper bath and is closed again as it leaves it. The mold and billet are then lowered into a second copper bath which has a very much lower temperature and the mold is this time filled with copper and is closed and withdrawn from the bath in that condition and allowed to cool. The copper-covered steel billet is then pushed out of the mold and heated and rolled into rods which are afterwards drawn into wire.

The object in having the first copper bath at so high a temperature is stated to be the hastening of the formation of a film of adherent copper-iron alloy. The reason for casting the greater part of the copper at the ordinary casting temperature, which is about 200° above its melting point, is that it is then possible to keep the copper from rapid oxidation and also, which is more important, to prevent the speedy contamination of the bath with copper and iron alloy. Numerous experiments made by the writer have shown that copper at 2550° F. dissolves solid steel, or alloys with it, with remarkable rapidity, thus making the copper unfit for use as a part of an electrical conductor.

(2) The welding process of uniting copper and steel is carried out as follows: Soft steel billets, approximately 3 1/4 inches in diameter by 72 inches long, are carefully freed from scale and are electro-plated with copper. They are then enclosed in neatly fitted cast copper tubes having walls of such thickness as to furnish approximately 25 per cent of copper in the composite blank, the total weight of each blank being approximately 200 pounds. The use of copper tubes gives a uniform product not otherwise obtainable. In order to exclude the air the blanks are coated at the ends with a fire-resistant paste. They are then heated to a temperature approximating 950° C. (1742° F.), this being sufficient to render both metals plastic. Each blank is then rolled in such a way that it is given a strong and uniform rolling pressure at all points, while the metals still retain a large part of their original heat. It has been found that the welding operation is completed within 50 seconds from the time the composite blank leaves the heating furnace and that the original 6 foot billet is extended in 1 3/4 minutes to a 25 foot wire bar 1 3/4 inches square. During the first few passes there is a slight extrusion of copper from the ends of the composite blank; the remainder, however, is securely welded and the small

extruded portions are sheared off from the finished wire bar.

These wire bars are reheated and rolled into coils of 3/4 inch wire rods. These are freed from oxide by pickling and are subsequently drawn cold into wires of any desired fineness (Fig. 13).



FIG. 13.—IN STORE-ROOM AT WIRE MILL
Copper-Clad Wire Bars in Foreground. Coils of Copper-Clad Wire and Cable

It is remarkable that the copper after it is welded to the steel by the preliminary rolling process adheres firmly to it and extends evenly with it through the various processes of hot rolling, cold drawing, annealing, etc. There is a strong stripping force in wire drawing which would instantly remove the copper jacket if it were not securely united to the steel. The writer had the opportunity of observing the drawing of copper-clad wire of many sizes, from 0.30 inch in diameter to 0.003 inch, the latter being as fine as hair (samples shown). No stripping took place in any case and the finest wire showed by chemical analysis that the copper covering still maintained nearly the same ratio to the steel core which existed in the original wire bar. Wire drawing may be likened to stripping tendency to the drawing of a lead pencil through a hole of the size of the graphite core only.

Supplementing this evidence of secure union of the two metals by the "welding" process is the fact that numerous heating, quenching, and twisting tests of welded copper-clad wire of all sizes produced no separation of copper from steel.

PROPERTIES AND USES OF COPPER-CLAD STEEL

The principal use of copper-clad steel at the present time is for electrical conductor wire of which over 10,000,000 pounds have been made by one manufacturer. It is used under conditions where a combination of high tensile strength and elasticity with sufficient conductivity is needed. This is particularly the case with uninsulated line wires for telegraph, signal, and telephone service, and with insulated "drop wires" running from poles to subscribers' houses in telephone practice. Even hard-drawn copper wire has not sufficient mechanical strength for such uses unless it is employed in larger sizes than can well be afforded. Iron or steel conductors have been used, but they rapidly deteriorate when in contact with the air, whereas copper-clad steel is as durable as the copper itself.

The elastic limit or point at which permanent stretching begins in the case of pure copper wire is so low that wind strains cause a sagging which must be taken up

¹ THIS JOURNAL, 1, 670.

and which eventually causes breakage. The most rapid destruction occurs, however, when copper wires are exposed to snow and ice in winter. Great losses occur through breakage of the wires and interruption of communication. (Sagging and breaking of copper-clad wire shown by slides.)

The judicious substitution of copper-clad steel wires for copper wires has done away with much of the trouble formerly experienced in the maintenance of telegraph, telephone, signal, power, and lighting wire circuits.

The grade of copper-clad wire most used has a conductivity averaging 30 per cent of the conductivity of pure copper wire; at the same time its tensile strength is 70 per cent greater and it is possible to apply 150 per cent greater tension before permanent stretching occurs. Its weight is 10 per cent less than that of copper wire of the same size and it has 100 per cent greater conductivity than either steel or iron (Table V).

TABLE V—PROPERTIES OF STANDARD COLONIAL COPPER-CLAD WIRE AND HARD-DRAWN COPPER WIRE

Size B. and S. G.	Average resistance at 60° F. in ohms per M. ft.		Weight per M. ft. in lbs.		Average breaking weight in lbs.	
	Bare, hard drawn					
	C. C. C.	H. D. Copper	C. C. C.	H. D. Copper	C. C. C.	H. D. Copper
0000	0.1603	0.04906	584	641	9805	7914
000	0.2021	0.06189	463	509	8250	6533
00	0.2549	0.07803	366	403	6830	5365
0	0.3214	0.09831	291	320	5680	4386
1	0.4052	0.1241	230	253	4800	3565
2	0.5110	0.1565	184	202	3900	2892
3	0.6443	0.1972	145	159	3200	2338
4	0.8124	0.2488	114.5	126	2630	1890
5	1.025	0.3138	91.0	100	2160	1520
6	1.292	0.3955	72.0	79	1770	1221
7	1.629	0.4986	57.7	64	1450	984
8	2.054	0.6288	45.5	50	1180	788
9	2.590	0.7934	35.5	39	965	630
10	3.267	0.9996	29.0	32	790	506
11	4.118	1.262	22.8	23.5	645	403
12	5.195	1.591	18.2	20.0	525	318
13	6.548	2.003	14.3	16.5	430	257
14	8.258	2.527	11.3	12.4	350	202
15	10.41	3.185	9.0	10.0	280	165
16	13.13	4.022	7.2	7.9	230	128
17	16.56	5.059	5.6	6.2	185	102
18	20.88	6.392	4.4	4.8	150	83
19	26.33	8.057	3.5	3.9	120	64
20	33.22	10.14	2.82	3.1	100	51

The tensile strength of copper-clad wire varies from 60,000 pounds per square inch in 0000 wire (0.46 inch in diameter) to 98,000 pounds per square inch in the case of No. 10 wire (0.102 inch in diameter), the actual breaking weights in the two cases being 9,805 pounds and 790 pounds, respectively. It is an interesting thing to know that the average breaking weight of copper-clad wire is from 3 to 6 times as great as the weight of a mile of the same wire, and the elastic limit is sufficiently high so that if wind and ice were not to be allowed for, there could be spans of a mile and more in length in the case of river crossings, etc. Tables VI and VII show relative costs for equal strengths and relative strengths for equal size.

Copper-clad wire is also used for trolley wire, springs, anchor bolts, pump rods, cotter pins, etc. Copper-clad wire (bare) has been successfully used for field

work in military, telephone, and telegraph service.

Its use has been suggested for small angle irons in skylights and other windows. It has not yet been extensively applied in building construction, but its great durability entitles it to wider use, especially for roofs, cornices, rain-water conductors, etc. The results of exposure tests of copper-clad sheet steel in the Pittsburgh atmosphere have been most encouraging.

WEATHER RESISTANCE OF COPPER AND COPPER-CLAD SHEET STEEL

Samples of sheet of copper and of steel coated with

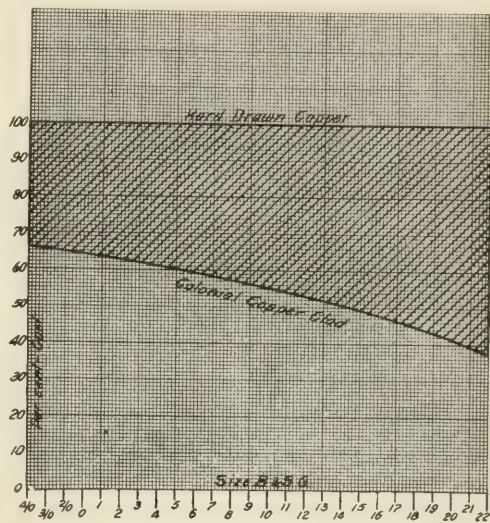


TABLE VI—COMPARISON OF COSTS FOR EQUAL STRENGTH (BARE WIRE—HARD DRAWN)

For equal strength values, this diagram gives the approximate relative costs per mile of the two materials, in bare form, hard drawn

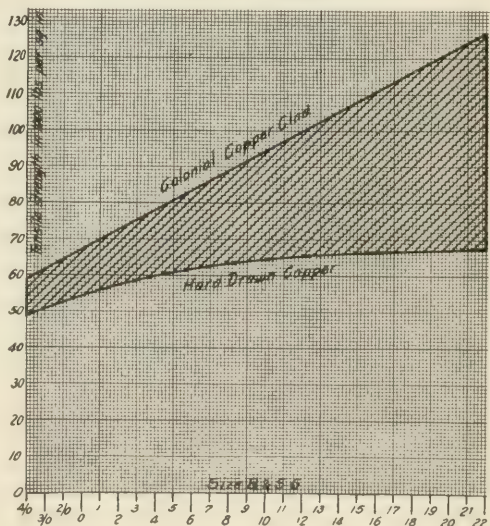


TABLE VII—COMPARISON OF STRENGTHS FOR EQUAL SIZE (BARE WIRE—HARD DRAWN)

For equal sizes, this diagram gives the actual strengths of the two materials, in bare form, hard drawn

the same grade of sheet copper by the Griffith process, and a sample of sheet made from a Colonial copper-covered wire bar were exposed on the roof of the Pittsburgh Testing Laboratory building from November 21st, 1911, to August 12th, 1913. The sheets were held in a flat position on a wooden base by means of screw hooks. This arrangement permitted the retention of moisture under the sheets and favored the starting of decay of the wood at those points. The sheets were in no case held so tightly that dust was excluded and slag dust from the roof coating blew in and cemented itself to the sheets in some cases.

The sheets were measured and weighed before exposure. The samples exposed were as follows:

- A. Copper-clad, one side. 1st lot Griffith.
- B. Copper-clad, both sides. 1st lot Griffith.
- C. "Lake" copper sheet used for welding to steel in making A, B, D, and F.
- D. Copper-clad, one side. 2nd lot Griffith.
- E. Copper-clad sheet made from one and three-fourths inch wire bar C-17.
- F. Duplicate of A, but exposed with steel side up.

	Weight Grams	WEIGHT AND SIZES Thickness, inch		Size, feet	Area Square inches
		Iron	Copper		
A.....	3730.6	0.060	0.005	2.97 × 1.09	466.56
B.....	5317.7	0.071	0.006	2.42 × 1.525	531.36
C.....	274.58	...	0.04	1.09 × 0.31	48.66
D.....	2853.8	0.026	?	4.59 × 0.92	680.11
E.....	1067.42	0.060	(incl. Cu)	2.05 × 0.49	144.65
F.....	3773.1	0.059	0.004	3.0 × 1.1	475.2

LOSS OF WEIGHT DURING EXPOSURE OF 21 MONTHS AND 20 DAYS

	Original weight Final weight Loss in weight		
	Grams	Grams	Grams
A.....	3730.6	3317.0	413.6
B.....	5317.7	5277.0	40.7
C.....	274.58	274.3	0.28
D.....	2853.8	2038.0	815.8
E.....	1067.42	1067.0	0.42
F.....	3773.1	3355.0	418.1

These results show the remarkable durability of copper and of copper-clad steel. (Specimens shown.)

Sample *E* is the only one which really represents the protecting efficiency of copper at the edges as well as on both surfaces. The long edges were copper clad but the ends were sheared. There was no extraordinary penetration of iron rust at the sheared ends. The only defects were some blisters developed by the crude way of working the wire bar into sheets. Slight rusting occurred at those exposed points but nowhere else, and the total amount of rusting was very insignificant. No tendency was observed for the rusting to penetrate under the copper and push it up. The same was true as to the places where the steel was exposed in drilling holes for holding the sheet in position. The total loss in weight in two years was insignificant, amounting to only a fraction of a gram, or less than 0.05 per cent.

The durability of Sample *C*, the copper sheet, is especially remarkable considering the acidity of the Pittsburgh atmosphere. The loss amounted to only 0.28 gram, approximately 0.1 per cent. The determination of total oxygen showed that the oxidation had penetrated less than 0.0002 inch or 0.5 per cent of the thickness of the sheet.

Samples *A* and *F* represented rather imperfectly

made specimens of copper-clad steel made by the Griffith process, *A* being intentionally left with exposed steel projecting at edges and ends in order to show the manner in which the steel corroded at and near the contact of copper and steel.

The loss of weight of both sheets was practically the same although *A* was exposed with the copper side up, and *F* with the steel side up. This seems to show that moist air rather than rain controlled corrosion of both steel surfaces. No perforation took place at any point of the copper surfaces on *A* or *F*. There was no special grooving to indicate electrolytic corrosion such as would be expected if the copper were not securely welded to the steel. The large losses in weight were due to the rusting away of the exposed steel (Fig. 14).

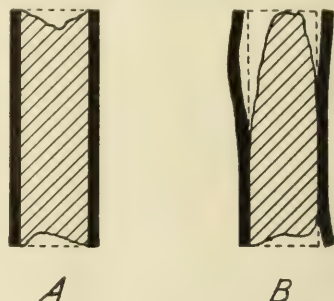


FIG. 14.—DIFFERENCE IN CORROSIONS OF STEEL SHEETS, COPPER-CLAD VS. COPPER-CASED

- (A) Cross-section Showing Corrosion of Steel at Edges Only—Copper Well Joined to Steel
- (B) Cross-section Showing Corrosion of Steel on Sides—Copper Separated from Steel

Sample *B* was coated with copper on both sides by the Griffith process, the short ends being sheared, but the steel extended 0.4 inch beyond the copper on one of the long sides. There were no perforations of the copper, and the loss in weight was caused by the rusting of the exposed steel at the edge.

Sample *D*.—During the first part of the exposure of this sheet a number of pin holes in the copper near one end were observed. Instead of extending by electrolytic action, these pin holes apparently were soon sealed up and were not observable at all, either as blisters or pits at the end of the period of exposure. This is quite contrary to what might have been predicted by one who considered the union between the copper and the steel a purely mechanical one.

While these experiments were in a way quite crude, they show conclusively the remarkably efficient protecting power of copper for steel to which it is welded. It is all the more remarkable when it is considered that the exposures were made in the moist and acid Pittsburgh atmosphere. Attention is called in this connection to the absence of electrolytic corrosion phenomena when copper and iron were securely welded.

The method of manufacturing these steel sheets was the Griffith process of welding copper to steel, slabs of soft steel being cleaned and electro-plated with copper and fastened securely to copper sheets of the desired thickness, the combined metals being then heated up

to a proper welding temperature and united by rolling to the required dimensions. Such sheets, of course, can be given any finish which is desired. They may either have a high polish and considerable stiffness or they may be made soft and pliable. If used for flat roofing sheets a higher temperature will be required for brazing together than is required for soldering either terne or tin plate. If used as corrugated sheets no brazing would be required.

There is no good reason, we believe, why a process of coating sheets with copper should not be developed along the lines of the present processes of tinning and galvanizing, and such copper-clad sheets could be more cheaply manufactured, but it would be naturally expected that as the coating would consist almost entirely of copper-iron alloy, it would be less durable than the pure copper coating made by the process of welding without melting.

POTASSIUM CYANIDE SOLUTION AS AN ETCHING MEDIUM AND SOLVENT FOR THE COPPER ON COPPER-CLAD STEEL

A boiling 25 per cent solution of potassium cyanide in distilled water was found to be a fairly rapid solvent for copper and its action upon steel is negligible.

It was accordingly used by the writer for investigating differences in coatings of copper-clad steel wires. The purest coatings dissolved most slowly and most uniformly, remaining bright. Impure coatings dissolved rapidly, developed a grooved structure, and if iron was present in material amount, the coating turned grayish black. In the case of coatings high in iron (12 per cent), the iron separated as a felt-like substance when the copper dissolved. (Samples of wire stripped of Cu by KCN were shown.)

The following experiments illustrate the solubility of iron and copper in dilute potassium cyanide solution:

SUBSTANCE	Weight Gram	Time boiled Minutes	Weight dissolved Gram	SOLVENT
Sheet steel.....	0.7400	30	0.0006	50 cc. 10% KCN
Copper foil.....	0.0950	30	0.0106	50 cc. 10% KCN
Copper foil in contact with steel.	0.0854	Cu 30	0.0782	50 cc. 10% KCN
	0.7080	Fe 30	0.0006	50 cc. 10% KCN

The more rapid solution when iron was in contact with copper was very striking.

The fact that an impure copper coating dissolves more rapidly is shown by the following comparison of two copper-clad wires.

		COPPER DISSOLVED				
	Weight	1st	2nd	3rd	4th	5th
	Grams	boil	boil	boil	boil	boil
	Grams	Grams	Grams	Grams	Grams	Grams
"Welded".....	299.0	9.0	11.0	14.0	15.5	14.5
"Alloyed".....	302.0	11.0	17.0	16.0	18.0	23.0

As an etching medium, potassium cyanide solution at ordinary temperature developed differences in copper coatings with and without iron, but it was particularly successful in bringing out the coarse structure produced in cast copper by the presence of arsenic.

In the following comparison No. 3 showed a fine grain and bright color when etched, No. 1 a distinct

coarse and slightly darker one, and No. 2, with 0.41 per cent arsenic, was very dark and very coarsely crystalline:

	1	2	3
Copper.....	99.76 %	99.48 %	99.90 %
Arsenic.....	0.062	0.412	0.005
Oxygen.....	0.085	0.024	0.065
Electrical conductivity.....	82.75	44.75	97.9

For these analyses and the specimens of cast copper, the writer is indebted to Mr. G. L. Heath, Chief Chemist of the Calumet and Hecla Copper Company.

SUMMARY

Copper may be united to steel by alloying or welding. In the former method the copper is melted. In the latter it is plastic only: 950° C. is a favorable temperature for welding. Both methods, if properly carried out, give mechanically secure unions. The welding process is most satisfactory for the manufacture of copper-clad wire because the conductivity is not diminished by the presence of copper and iron alloys. Melted copper dissolves iron very rapidly. The resultant alloys are poor conductors of electricity. Iron and copper form an alloy if heated together in a non-oxidizing atmosphere to a point just above the melting point of copper. If heated hotter, alloy formation proceeds more rapidly.

Copper is extraordinarily resistant to atmospheric corroding influences. Tests of copper-clad sheet steel in Pittsburgh showed very little effect on the copper in twenty-two months. Copper is more expensive than zinc but costs only 40 per cent as much as tin. It is more durable than either. Combinations of copper and steel should be more widely used. Steel welded to copper does not corrode more rapidly than does the same steel entirely out of contact with copper.

Potassium cyanide in 25 per cent aqueous solution dissolves copper and barely attacks iron. It is useful as a solvent and as an etching medium for copper-clad steels and as an etching medium for cast copper containing arsenic.

BIBLIOGRAPHY OF PATENTS COVERING UNIONS OF COPPER OR ITS ALLOYS WITH IRON OR STEEL, BY THE AID OF HEAT

UNITED STATES PATENTS

- Method of Coating Iron with Brass or Copper. 11,319. July 18, 1854. H. Burgess.
 Improvements in Coating Metals. 21,797. 1858. Hiler.
 Improved Process of Uniting Steel with Copper, Brass, Etc. 39,531. August 11, 1863. R. Savary.
 Improvement in Line-wires for Telegraph. 47,940. 1865. Farmer and Milliken.
 Improvement in Line Wire, for Telegraphs. 59,763. 1866. Farmer and Milliken.
 Improved Mode of Uniting Steel or Iron with Copper. 69,001. September 17, 1867. E. T. Ligon.
 Improvement in Combining Copper with Cast Steel. 73,375. 1868. Park.
 Improvement in Telegraph Wire. 91,416. June 15, 1869. A. Cary.
 Machines for Above Process. 91,417. Cary.
 Plating Iron for the Manufacture of Hinges. 98,354. December, 1869. J. J. and L. Crooke.
 Improvement in Welding Brass or Alloy of Copper to Iron or Steel. 126,894. May 21, 1872. G. R. Meneely.
 Improvement in Plating or Coating Metals. 130,362. August 13, 1872. E. E. de Lobstein.
 Improvement in Coating Metals with Copper. 141,132. July 22, 1873. O. Gauduin, J. B. J. Mignon, and S. H. Rouart.

- Coating Iron Surfaces. 227,268. May 4, 1880. I. Kintz.
- Method of Plating Iron and Steel. 242,194. May 31, 1881. T. Flattman.
- Manufacture of Copper Plated Sheet Iron. 244,240. July 12, 1881. C. Haegeler.
- Mode of Plating Iron or Steel. 258,119. May 16, 1882. H. Rensch.
- Plating Metals. 267,879. November 21, 1882. C. Haegeler.
- Mode of Plating Iron and Steel. Reissue 10,367. August 14, 1883, of Patent 258,119 of May 16, 1882. H. Rensch.
- Process of Making Electric Conductors. 286,796. October 16, 1883. T. Egleston.
- Manufacture of Metal. 286,904. October 16, 1883. G. H. Chinnock.
- Compound Electrical Conductor. 288,443. November 13, 1883. L. Johnson.
- Manufacture of Electrical Conductors. 296,074. April 1, 1884. T. Shaw.
- Method of Plating Metals. 303,025. 1884. McCleane and Grey.
- Manufacture of Compound Wire. 309,468. December 16, 1884. I. A. and M. D. Kilner.
- Apparatus for Manufacturing Compound Telegraph Wire. 310,993. January 20, 1885. Farmer.
- 310,994. Modification of 310,993.
- Process of Manufacturing Compound Telegraph Wire. 310,995. 1885. Farmer.
- Electrical Conductor. 312,673. February 24, 1885. C. M. Thompson and C. B. Eberle.
- Method of Making Electrical Conductor. 320,684. June 23, 1885. W. S. Platt.
- Method of Constructing Compound Metallic Bodies. 361,799. April 26, 1887. E. Wheeler.
- Process for Coating Iron with Tin or its Alloys or Other Metals. 371,248. October 11, 1887. E. I. Braddock.
- Ingot for the Manufacture of Compound Metallic Tubes. 371,719. October 18, 1887. T. S. Very.
- Telegraph Wire. 379,535. March 13, 1888. W. Hewitt.
- Manufacture of Wire. 410,368. 1889. Martin.
- Plated Wire. 441,885. December 2, 1890. G. U. Meyer.
- Process of Making Plates, Etc., of Combined Metals. 530,719. December 11, 1894. A. Rodig.
- 543,192. Extension of 530,719 to cover over-hanging projection or holding fast to cast material.
- Method of Making Compound Wire. 550,705. December 3, 1895. H. E. Williams.
- Process or Method of Welding Copper upon Steel. 577,817. February 23, 1897. J. Burns.
- Uniting or Welding Metal. 580,344. April 6, 1897. Griffith.
- Current-Conducting Rail for Electric Railways. 588,541. August 17, 1897. L. E. Walkins.
- Method of and Apparatus for Welding Metals. 593,534. November 9, 1897. J. W. Comley.
- Manufacture of Electric Conductors. 628,770. July 11, 1899. S. O. Cowper-Cowles.
- Process of Welding Steel and Copper. 673,664. May 7, 1901. T. Smith and F. G. Sherry.
- Tube. 674,394. May 21, 1901. A. E. Beck and G. Townsend.
- Uniting or Welding Metals. 685,758. November 5, 1901. Griffith.
- 688,162. December 3, 1901. J. W., R. W., and C. H. L. Comley.
- Plating Metal. 704,793. July 15, 1902. Griffith.
- Process of Coating Tubes. 708,788. 1902. Wachwitz.
- Process of Uniting Metals. 729,113. May 26, 1903. J. M. Anderson.
- Metal-Welding. 776,706. December 6, 1904. Wachwitz.
- Electrical Conductor. 750,509. 1904. Wherry.
- Process of Uniting Two Metals. 750,511. 1904. Wherry.
- Flux. 750,512. 1904. Wherry.
- Art of Uniting Metals. 789,530. May 9, 1905. W. L. Fenn and J. W. Conway.
- Art of Making Copper-Coated Iron or Steel Sheets. 827,378. July 31, 1906. W. P. Lewis.
- Ship's Plate. 851,069. April 23, 1907. J. Craig.
- Process of Making Compound Metal Bodies. 851,684. April 30, 1907. Monnot.
- Process of Producing Compound Metal Bodies. 853,716. 1907. Monnot.
- Process of Making Bimetallic Products. 853,932. 1907. Monnot and Martin.
- Manufacture of Compound Pipes and Tubes. 860,232. July 16, 1907. J. W. Offutt.
- Electric Conductor. 867,659. October 8, 1907. W. Hoopes.
- 878,984. Extension of 851,684. Monnot.
- 893,932. July 21, 1908. Monnot.
- 894,163. Extension of 894,162 to cover two coatings on the core. Monnot.
- Same as above, to include silver. 894,164. Monnot.
- Process of and Apparatus for Making Compound Metal Objects. 908,858. December 1, 1908. Monnot.
- Process and Apparatus for Producing Compound Metal Objects. 910,408. January 19, 1909. Monnot.
- Process of Making Clad Metal Articles. 927,371. 1909. Monnot.
- Clad Metal. 927,372. 1909. Monnot.
- Clad Metal and Process of Producing Same. 929,687. 1909. Monnot.
- Mold for Rail Bonds. 918,108. 1909. Wherry.
- Method of Uniting Metals. 959,517. May 31, 1910. Griffith.
- Compound Metal Object. 960,372. June 7, 1910. Monnot.
- Electrolyte for Depositing Copper. 976,454. 1910. Grey and Griffith.
- Method of Uniting Metals. 976,455. November 22, 1910. Grey and Griffith.
- Method of Making Homogeneous Mechanical Juncture. 1,012,077. 1911. Herrick.
- 1,065,727. 1913. Rockey and Eldridge.

BRITISH PATENTS

- A Method of Covering or Coating Iron, Steel or other Metals, or Mixtures of Metals. 4,053. 1816. J. Dayman.
- Plating Iron and Steel with Brass and Copper, and Forming the Same into Plates, Bars, Etc. 4,598. 1821. J. Poole.
- 5,111. 1825. D. Gordon and W. Bowser.
- Coating Iron and Other Metals. 8,403. 1840. J. B. Neilson.
- Manufacture of Metals and Coating Iron and Steel. 11,971. 1847. A. Parkes.
- Coating Iron and Other Metals. 12,993. 1850. E. G. Pomeroy.
- Coating Iron with Copper and Brass. 421. 1853. Burgess and Watt.
- Covering Iron with Copper or Copper Alloys. 709. 1855. Tytherleigh.
- Coating Iron with Copper or its Alloys. 923. 1856. Tytherleigh.
- Rollers for Printing Fabrics. 1,924. 1856. Tytherleigh.
- (Provisional) Preparing and Coating Metallic Surfaces. 2,472. 1856. R. D. Atkinson.
- Improvement in Coating or Amalgamating Metals. 1,100. 1858. Hilier.
- Improvements in Coating Iron and Steel. 3,475. 1862. W. and H. Bowser.
- Improved Process for Coating Iron. 841. 1863. W. Mitchell.
- Coating Ship Surfaces with Copper, Brass, Etc. 351. 1864. M. C. de C. Sinibaldi.
- Coating Iron and Steel. 598. 1869. G. J. Hinde.
- Improvements in Coppered Iron or Sheet Steel. 3,466. 1871. Lake.
- Copper Covered and Copper Cored Wire. 1,847. 1872. W. R. Lake.
- Depositing Copper on Iron and Steel. 3,970. 1872. Johnson.
- Improvements in Materials for Casks, Etc. 1,887. 1875. A. B. Walker.
- Coating Metals. 1,836. 1881. F. C. Glaser.
- Coating or Plating Certain Metal Surfaces. 3,122. 1882. A. M. Clark.
- Coating Iron and Steel Sheets, with Copper and Copper Alloys. 10,886. 1884. J. and J. Taylor.
- Method and Apparatus for Manufacturing Compound Telegraph Wire. 798. 1885. Allison.
- Process for Plating Metals and Metallic Alloys. 3,985. 1886. C. E. Steinweg.
- Improvements in the Manufacture of Wire. 6,834. 1887. A. Mannesmann.
- Coating Iron and Steel Plates with Copper. 17,269. 1888. G. Prout and D. Murray.
- Coating of Metals. 3,149. 1889. A. J. Boulton.
- Coating Sheet Iron with Copper or Brass. 4,335. 1889. W. E. Everitt.
- Flux for Welding Copper and Steel. 9,187. 1889. H. H. Chandler.
- Manufacture of Band, Plates, Sheets, Etc., of Combined Metals. 17,009. 1891. Martin.
- Improvement in the Manufacture of Plates Having a Partial Coating of Other Metal. 21,467. 1892. L. Grambow.
- Coating Iron and Steel with Brass and Other Metallic Alloys. 1,906. 1893. A. V. C. and J. B. Fenby and G. Moore.
- Coating Iron and Steel with Copper or an Alloy of Copper. 29,251. 1896. R. D. Burnie and W. T. Lougher.
- Process and Apparatus for Uniting Metal Sheets, Bars, Etc. 26,030. 1897. Comley.
- Improvement Relating to Uniting or Welding Metals. 8,780. 1897. Griffith.
- Protecting Tubes of Steam Generators by Application of Silver. 9,057. 1899. E. J. M. la Combe.
- Uniting Copper and Copper Alloys with Another Metal (Iron or Steel) 10,763. 1899. W. G. Clark.
- Coating Metals. 11,603. 1900. Martin.

- Improvements of Boiler and Other Metal Tubes. 11,981. 1900.
 A. E. Beck and G. Townsend.
 Manufacture of Steel Ingots Plated with Copper. 16,993. 1902.
 S. Vanstone.
 Improvements in Manufacture of Hot Water Tanks, Etc. 15,383.
 1903. D. P. Menzies.
 Process of Uniting Metals. 18,454. 1903. J. D. Prince.
 Production of Metallic Protective Deposits on Metals. 9,836. 1904.
 A. Lévy.
 Manufacture of Bimetallic Ingots. 12,000. 1904. H. Harmet.
 Uniting Iron and Steel with other Metals. 17,660. 1904. Davies
 and Clark.
 Improvement in Manufacture of Compound Metal Ingots, Etc. 8,913.
 1906. Monnot.

GERMAN PATENTS

- Method of Manufacture of Conductor Wire with Metallic Covering.
 47,950. 1888. Martin and Martiny.
 Method for Coating One Metal with Another. 124,898. January 4,
 1899. S. H. Thurston.
 Manufacture of Sheet Steel with Copper Covering. 124,387. 1900.
 Martin.
 Process for Welding Baser Metals for Purposes of Plating. 137,017.
 1902. Wachwitz.
 Process for Uniting Steel and Other Metal Plates with Aluminum, Etc.
 152,042. 1903. Wachwitz.

FRENCH PATENTS

- Improvements in the Manufacture of Wire. 168,133. 1885. Martin.
 Supplement. Perfected Method of Making Bimetallic Wires. 168,133.
 1888.
 Bi-Metal Sheets and Plates, Process of Manufacture of. 206,789.
 1890. Martin.
 Perfected Process for Making Bimetallic Wires. 213,109. 1891.
 Martin.
 Manufacture of Bimetallic Bands, Plates, Sheet Iron and Hoops.
 216,565. 1891. Martin.

BELGIAN PATENTS

- New Process of Manufacturing Bimetallic Plates and Wires.
 171,442. 1903. Martin.

DEPARTMENT OF RESEARCH AND CHEMICAL ENGINEERING
 PITTSBURGH TESTING LABORATORY

THE CONDENSATION OF GASOLINE FROM NATURAL GAS¹

By GEORGE A. BURRELL AND FRANK M. SEIBERT

In this paper are given some results of work performed by the Bureau of Mines having to do with the condensation of gasoline from natural gas.

CHEMISTRY OF NATURAL GAS

With the growth of the natural gas gasoline industry natural gases have been classified into two divisions so called "wet" and "dry" gases, depending upon whether or not gasoline can be commercially condensed from them. The classification is exceedingly loose because natural gas mixtures may range from those containing only methane as the combustible constituent (a gas difficult to liquefy) to those in which the hydrocarbon vapors predominate and which liquefy easily. Between the two extremes there are natural gases containing the different constituents, methane, ethane, propane, butanes, pentanes, etc., in many different combinations. Some of these may not contain enough of the desirable gasoline constituents for commercial purposes, others may.

Natural gases not found intimately associated with oil are the so-called "dry" gases. Those found in the same strata with oil and in intimate contact with the same are those from which gasoline is obtained in the natural gas gasoline industry. The Bureau of Mines finds as the result of many analyses that natural gases

¹ Paper presented at the 48th meeting of the American Chemical Society, Rochester, September 8-12, 1913. Published by permission of the Director of the Bureau of Mines.

are mixtures in which hydrocarbons of the paraffin series predominate and that small quantities of nitrogen, carbon dioxide and water vapor are present. Hydrogen sulfide is sometimes present; perhaps other sulfur compounds too. F. C. Phillips found natural gases of Western Pennsylvania, which he worked with, to contain paraffin hydrocarbons, carbon dioxide and nitrogen. Other investigators invariably report at least small proportions of carbon monoxide, hydrogen and ethylene. Experimental errors in the work easily accounts for these errors. The authors of this paper believe the work of S. A. Ford as showing very large percentages of hydrogen to be in error. His analyses have been quoted many times in different text books. They were made in 1885. The authors of this paper in looking over the analyses made by them of thirty natural gas samples collected from different parts of the country find the heating value ranging from 685 B. t. u. to 1577 B. t. u. per cubic foot at 60° F. and 760 mm. pressure. These analyses will be incorporated with many others in a government publication. These gases range from marsh gas issuing from the marsh beds, and containing only methane as the combustible gas to casing head gases that are used for lighting and heating towns. Only two of the gases, those of the highest heating value, are probably adapted for gasoline condensation. One sample contained (as shown by combustion analysis) in addition to methane, carbon dioxide and nitrogen, 75.16 per cent of ethane. The natural gas of Pittsburgh has a gross heating value of about 1177 B. t. u. per cubic foot at 0° C. and 760 mm. pressure.

SIGNIFICANCE OF ORDINARY ANALYTICAL RESULTS

In the analysis of natural gases by the slow combustion method, the data obtained admit of the calculation of only two of the chief constituents. The mixture, however, may contain all of the gaseous paraffins and considerable quantities of the vapors of the liquid hydrocarbons. When the lower members of the paraffin hydrocarbons predominate, the results obtained are more accurate than when the higher members predominate. Natural gases from which gasoline can be extracted contain appreciable quantities of the liquid hydrocarbon vapors. In the analyses of these mixtures the ordinary slow combustion analysis will give only approximate results for several reasons.

First—The gas mixture often contains more than two combustible constituents.

Second—Some of the gases and vapors deviate considerably from the gas laws and their true molecular volumes¹ are unknown.

Third—So small an amount of the mixture must be used in some cases that experimental errors are greatly magnified in calculating to a percentage basis.

Typical analyses of two different natural gases follow which contain small amounts of methane and larger amounts of ethane, propane and butane with the vapors of the liquid hydrocarbons pentane, hexane, etc. These analyses serve to show how approximate a com-

¹ A government publication by the authors which covers this question is in press.

bustion analysis may be even when the analysis is carefully performed.

In the analysis of gases of this type the explosion method is entirely out of the question. The analyses were made by the method of slow combustion. Duplicate analyses were made of each sample.

SAMPLER No. 1

	I Cc.	II Cc.
Volume of sample taken	20.00	19.95
Oxygen added	95.70	95.30
Total volume	115.70	115.25
Volume after burning	64.10	64.00
Contraction due to burning	51.60	51.25
Volume after CO ₂ absorption	22.10	22.60
Carbon dioxide produced by burning	42.00	41.40

RESULTS OF ANALYSES	PER CENT	
Ethane	96.00	98.75
Propane	6.00	3.33
Total paraffins	102.00	102.08

SAMPLE No. 2

	III Cc.	IV Cc.
Volume of sample taken	20.35	23.50
Oxygen added	96.15	126.75
Total volume	116.50	150.25
Volume after burning	60.10	85.30
Contraction	56.40	64.95
Volume after CO ₂ absorption	10.40	28.26
Carbon dioxide produced by burning	49.70	57.10

RESULTS OF ANALYSES	PER CENT	
Ethane	65.85	66.80
Propane	37.50	36.50
Total paraffins	103.35	103.30

The foregoing analyses show how a small difference in the contraction due to combustion and the carbon dioxide produced will, when calculated to the same basis, affect the distribution of the paraffins and also the total paraffin content. The fact that the gases total over 100 per cent is because the correct molecular volumes of all the gases present in the mixtures are not known. For example, in the case of analyses I and II (duplicate analyses) the contraction in I is 51.60 cc. from 20.00 cc. of the original sample while the contraction in II is 51.25 cc. This latter result, when calculated to 20.00 cc. of sample, gives a difference of 0.22 cc. from the first, which is the experimental error.

The carbon dioxide produced in I from 20.00 cc. of sample is 42.00 while that produced from II when calculated to 20.00 cc. sample is 41.50 cc. or a difference of 0.5 cc., the experimental error.

The combined difference in the contractions and carbon dioxide change the paraffin distribution by 98.75—96.00 or 2.75 per cent in the case of ethane and 6.00—3.33 or 2.67 in the case of propane. The total paraffin hydrocarbon content is changed only by 102.08—102.00 or 0.08 per cent.

In a like manner in the case of analyses III and IV (duplicate analyses) the contraction produced in III by the combustion is 56.40 cc. with 20.35 of sample while the contraction produced in IV calculated to 20.35 cc. of sample is 56.25 cc. or a difference of 56.40 cc. — 56.25 cc. or 0.15 cc., the experimental error.

The carbon dioxide from 20.35 cc. of sample is 49.70 cc. in III while the carbon dioxide in IV is 40.44 cc. when calculated to 20.35 cc. of sample. This is a difference of 0.26 cc., the experimental error. Here the combined difference of the contractions and the carbon dioxide change the paraffin distribution by 66.80—65.85 or 0.95 per cent in the case of ethane and 37.50—36.50 or 1.00 per cent in the case of propane. The total paraffin content is changed only by 103.35—103.30 or 0.05 per cent.

Although combustion analysis shows only approximately the quantity of paraffin hydrocarbons present, the total paraffin hydrocarbons are correct or nearly correct. The same can be said of the heating value and specific gravity as calculated from the analyses. The ascertaining of the different hydrocarbons that may be found in natural gases has long been a stumbling block to gas analysts. The ordinary eudiometer analysis offers nothing in the way of a complete separation. The total paraffin hydrocarbon content with only an approximation of the individual paraffin has been the only end attained. The authors in working on the problem succeeded in making a separation of a natural gas into its individual paraffin hydrocarbons by means of fractional distillation at low temperatures. Natural gas was first liquefied by means of liquid air and then by means of a Töpler pump, the methane was removed. The vapor pressure of liquid ethane (boiling point —93° C.) is so small at the temperature of liquid air (—190° C.) that two fractionations sufficed to remove the methane, which was measured and analyzed. The residual gas was then subjected to a temperature of —130° C. and as much gas as could be removed was withdrawn with the pump. The mixture withdrawn proved to be ethane and propane. At —130° C. all the ethane (boiling point —93° C.) and part of the propane (boiling point —45° C.) is removed. This fraction was measured and analyzed. The residual liquid was then allowed to volatilize and was found to be propane. The proportions were then found by simple calculations. Butane was not found within the experimental error of the manipulation which was perhaps 0.2 or 0.3 per cent. Traces of butane exist in the gas, however, also of pentane and hexane. The complete analysis including the quantity of each paraffin hydrocarbon found by the above method follows. For comparison the ordinary eudiometric analysis of the natural gas is given: The natural gas is that used in Pittsburgh.

	By liquefaction fractionation Per cent	By eudiometric analysis Per cent
CH ₄	86.8	79.2
C ₂ H ₆	5.7	19.6
C ₃ H ₈	6.2	...
N ₂	1.3	1.2
Total	100.0	100.0

The carbon dioxide in the Pittsburgh natural gas amounts to a trace (0.03 per cent). The gas cannot be used for the commercial production of gasoline although it contains sufficient of the hydrocarbon vapors to produce some condensate (drip) in the pipe

lines. This is because of the immense volume of gas passing. The gas comes from W. Va. and is typical in composition of gases from that field that are supplying many towns. The natural gas from the Hogshooter Pool of Oklahoma, some of which goes to Kansas City, contains only methane (95.4 per cent) as the combustible constituent. The rest is nitrogen and carbon dioxide (dry basis). The Bureau has the composition of the natural gases that are supplying many towns. Further work is being done by the authors on the fractionation of natural gases. More difficulty is experienced in making a separation when all of the gaseous paraffins and vapors of the liquid ones are present.

OCCURRENCE OF GASOLINE IN NATURAL GAS

The yield of gasoline from natural gas is determined largely by the quantity of the liquid paraffin vapors in the permanent gases. Temperature and pressure conditions in the well, gasoline content of the oil, and intimateness of contact between oil and gas, all affect the yield. Such rapid expansion of a gas from a casing head may occur as to cause a heavy condensation of vapors at the casing head.

Methane (critical temperature $-95.5^{\circ}\text{C}.$, critical pressure 735 pounds per square inch) is always in a well in the gaseous condition. Ethane (critical temperature $35^{\circ}\text{C}.$, critical pressure 664 pounds per square inch) exists in some wells as a gas, in others, probably as a liquid. Propane and the butane are even more easily liquefied than ethane. In gases used for gasoline production they are present as gases. In such cases reduced pressures are usually applied to the wells. The gasoline vapors are mixed with these permanent gases in the same manner that moisture exists with air.

In gasoline plant operation, the pressure applied to condense the vapors must, of course, depend on the partial pressures of the vapors in the natural gas mixture. If butane (boiling point $1^{\circ}\text{C}.$) for instance constitutes twenty per cent of the mixture, there would be needed a total pressure of seventy-five pounds per square inch in order to have 15 pounds on the butane vapor, and cause condensation of the vapor to begin. For this reason one gas may produce condensate with 75 pounds, while another gas will need 200 to 300 pounds. In the standard type of cooling and pressure arrangement as used to-day, methane and ethane are not liquefied but some propane and butane are. In addition the final mixture as received at the collecting tank, will contain condensed gasoline vapors, *i. e.*, pentanes, hexanes, etc. There will also be found a portion of the gases methane and ethane dissolved in the liquids. In other words several changes will have taken place. One has to do with the condensation of vapor, another with the liquefaction of gas and another with the solubility of the permanent gases in the liquid produced. The three changes mentioned are so intimately connected with each other that one factor cannot be disturbed without affecting the others. For instance such a temperature and pressure could be employed as to increase the condensation of the desirable constituents (the gasoline

vapors) but with increasing pressure and lowered temperature more of the undesirable gaseous constituents would liquefy. These when exposed to atmospheric conditions of temperature and pressure would immediately volatilize, carrying with them some of the gasoline constituents. At increasing pressures more ethane and methane would be dissolved. With release of pressure they too would escape.

TESTING NATURAL GAS FOR GASOLINE VAPORS

Before plant installations are made for the purpose of extracting gasoline from natural gas an investigation of the several factors should be made. These include (1) quality of gas, (2) quantity of the gas, (3) disposal of product.

QUALITY OF GAS

Laboratory methods in use at the present time consist chiefly of combustion tests, solubility tests and specific-gravity tests. The combustion analysis gives only a rough approximation. The specific-gravity test is much used. Natural gases may range in specific gravity from about 0.56 to 1.50, compared to air. Some gases are used for condensing gasoline that have as low a specific gravity as 0.80. All gases of this specific gravity are not adapted, however. If the carbon dioxide or nitrogen content of a natural gas is high and not known, the specific gravity test may be misleading.

Alcohol, claroline oil, olive oil, kerosene oil, etc., all have been used for determining the solubility of natural gases. The higher members of the paraffin series are more soluble in these solvents than are the lower members. The authors have used tests that consist in shaking 100 cc. of the natural gas in 50 cc. of alcohol or 35 cc. of claroline oil, and noting the loss in gas volume. The test is arbitrary. Under these conditions it was found that natural gases soluble to the extent of from 30 to 86 per cent of their volume were used for condensing gasoline. In all these tests inconsistencies have been noted, so that especially as regards the minimum specific-gravity tests and solubility numbers herein given one would not feel sure about the feasibility of plant installation.

Natural gases differ much in composition. The so-called wet gases, for instance, might contain a very large proportion of methane, with but little ethane, propane and butane, but enough of the gasoline vapors to warrant plant installation. Another gas with the same specific gravity might contain a comparatively small proportion of methane and ethane, a large proportion of butane and propane but not enough of the gasoline constituents to warrant plant installation. The safest recourse is to be had to some type of laboratory compressor or better still to a portable outfit consisting of gas meter, gas engine, compressor, cooling coils and receiver. Such an outfit can be hauled from well to well on a wagon. Tests conducted by such a method must also be in the hands of competent persons.

QUANTITY OF THE GAS

Many plants are in operation working on as little as 125,000 cubic feet of gas per 24 hours. Some are

working on as little as 40,000 cubic feet. These latter are largely experimental. A fair sized plant to handle 125,000 cubic feet costs about \$10,000. There are probably 200 plants in the United States making gasoline from natural gas.

VALUE OF RESIDUAL GASES

Residual gases left after plant operation are of high heating value, unless contaminated with air. Air may leak into the pipes due to reduced pressure on the pipe lines (as much as 25 inches of mercury). In one case the authors found that a residual gas had a heating value almost twice as high as the heating value of the Pittsburgh natural gas. According to the facts already presented the residual gas is bound to be a

Table I gives the results of the analysis of the natural gas used by a plant near Follansbee, W. Va. The analysis, specific gravity and claroline absorption show this to be a rich gas. It will be seen that but little difference exists between the composition of the crude gas before and after it has been compressed to 50 pounds per square inch. It is only after compression to 250 pounds per square inch and cooling, that the composition of the gas mixture changes appreciably. The high heating value of the residual gas is apparent.

Table II shows the results obtained from a small plant near McDonald, Pa. This is not a very "wet" gas. Its claroline absorption number is rather low. It is probably near the lower limit of a gas adapted for the condensation of gasoline. The composition

TABLE I

Lab. No.	Kind of gas	Gross heating value 60° F. and 760 mm. Calculated	Specific gravity, Air = 1	Per cent absorbed by 35 cc. claroline oil	Composition, Per cent							
					Air calculated from C_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	N_2	CO_2	Total
2281	Natural gas from Follansbee, W. Va.	2339	1.41	83.6	21.4	78.2	0.4	(a)	100.0
2284	Residual gas after 50 lbs. compression.	2295	1.38	82.0	26.6	72.8	0.6	(a)	100.0
2286	Product has been removed.....				77.3	22.0	0.7	(a)	100.0
	Residual gas after 250 lbs. compression.	1913	1.15	63.6	77.3	22.0	0.7	(a)	100.0
	Product has been removed.....				77.3	22.0	0.7	(a)	100.0

(a) Trace of CO_2 present. Gas is from 75 producing wells and is withdrawn under a reduced pressure of 20 inches of mercury. The gasoline is blended with low-grade refinery naphtha and then marketed

rich gas, because the methane and the ethane are not liquefied, and only a portion of the propane and butane. Neither are all the gasoline vapors condensed. Air may appreciably lower the value of the gas, however. Some residual gases contain 40 to 50 per cent of air.

DEPLETION OF THE RESIDUAL GAS AS REGARDS QUANTITY

To give exact figures for the quantity of gas and vapor that disappear from the raw gas in plant operations is impossible. If four gallons of condensate are produced from each 1,000 cubic feet of natural gas, about 140 cubic feet of gas per 1000 may disappear.

of the gas does not change to a very marked degree after it has been compressed to 80 pounds per square inch.

NOTE

The foregoing is abstracted from a bulletin covering in greater detail the condensation of gasoline from natural gas. This bulletin is in press. It treats of the waste of natural gas, status of the natural gas gasoline industry, future of it, utilization of casing head gas, occurrence of gas and oil, use of gas from flow tanks, value of plant equipment, chemistry of natural gas, occurrence of gasoline in casing head gas, gasoline

TABLE II

Lab. No.	Kind of gas	Gross heating value 60° F. and 760 mm.	Sp. gr. Air = 1	Per cent absorbed by 35 cc. caroline oil	Composition, Per cent							
					Air calculated from C_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CO_2	N_2	Total
2809(b)	Natural gas, McDonald, Pa.	1719	1.01	38.5	2.7	96.1	1.0	0.2	100.0
		1204(b)	..	27.0	30.1	1.9	67.3	0.6	0.1	100.0
2807	Residual gas after 20 lbs. compression product has been removed.	1233	..	30.1	29.0	0.7	69.6	0.6	0.1	100.0
2809	Residual gas after 80 lbs. compression, product has been removed.	1164	..	25.0	30.0	7.2	62.0	0.7	0.1	100.0

(a) This analysis calculated air-free to show the composition of the crude gas. (b) Actual composition of gas delivered to the compressor.

This figure is based upon the equivalent of liquid butane, pentane, etc., in cubic feet of gas.

The following tables show the laboratory tests conducted on gases from two plants at various stages of plant operation. The Bureau has many more.

plant operation, testing natural gas for gasoline, value of residual gas, air in the gas, life of wells, handling and blending the condensate, and the marketing of the product.

BUREAU OF MINES
PITTSBURGH

SOME TESTS OF PAINTS FOR STEEL, SUBJECTED TO ALTERNATE EXPOSURE TO AIR AND FRESH WATER¹

By PERCY H. WALKER² AND S. S. VOORHEES³

The following joint investigation was planned by the Geological Survey, Department of the Interior, and the Bureau of Chemistry, Department of Agriculture, in response to general requests for definite information regarding effective paint coatings for the protection of structural steel, especially when subjected to intermittent water immersion. Before the work could be started, however, certain general investigations, in-

direction of the Bureau of Chemistry and the Bureau of Standards.

The general investigation considered the protection afforded by paint coatings to both wood and steel structures under varying conditions of service. Such a program, naturally resolved itself into a theoretical consideration of the agencies which cause corrosion and decay and means to prevent this action, and such theoretical conclusions had to be confirmed by an extended series of service tests before they could be accepted. A number of investigations and tests have

COMPOSITION OF PIGMENTS AND CONSTANTS OF THE LINSEED OIL

White Lead, Contract No. 8072:

Spec. gravity (15.6° C./15.6° C.).....	6.46
Total lead as PbO (per cent.).....	85.8
Carbon dioxide (CO ₂) (per cent.).....	12.7
Loss on ignition less CO ₂ (per cent.).....	1.6

The above analysis indicates the following composition:

Lead carbonate (PbCO ₃) (per cent.).....	76.9
Lead hydroxid [Pb(OH) ₂] (per cent.).....	23.1

Zinc White, American, Contract No. 2958:

Specific gravity (15.6° C./15.6° C.).....	5.56
Moisture (per cent.).....	0.2
Insoluble in HCl (per cent.).....	0.1
Lead.....	trace
Zinc oxid (ZnO) (per cent.).....	99.4

Lampblack, Contract No. 8128:

Specific gravity (15.6° C./15.6° C.).....	1.72
Moisture (per cent.).....	1.1
Ash (per cent.).....	0.07

Slag Pigment, Contract No. 10436:

Specific gravity (15.6° C./15.6° C.).....	3.51
Moisture (per cent.).....	0.2
Ferrous oxid (FeO) (per cent.).....	15.1
Ferric oxid (Fe ₂ O ₃) (per cent.).....	3.4
Alumina (Al ₂ O ₃) (per cent.).....	6.1
Manganese oxid (MnO) (per cent.).....	5.3
Silica (SiO ₂) (per cent.).....	13.0
Calcium sulphid (CaS) (per cent.).....	1.1
Lime (CaO) (per cent.).....	41.4
Magnesia (MgO) (per cent.).....	9.1
Phosphoric anhydrid (P ₂ O ₅) (per cent.).....	4.4

Flake Graphite, Contract No. 8129:

Specific gravity (15.6° C./15.6° C.).....	2.20
Moisture (per cent.).....	0.07
Ash (per cent.).....	6.8

Artificial Graphite, Contract No. 8123:

Specific gravity (15.6° C./15.6° C.).....	2.17
Moisture (per cent.).....	0.06
Ash (per cent.).....	7.2

Indian Red, Contract No. 8124:

Specific gravity (15.6° C./15.6° C.).....	5.12
Insoluble siliceous matter (per cent.).....	0.8
Alumina (Al ₂ O ₃) (per cent.).....	2.6
Ferric oxid (Fe ₂ O ₃) (per cent.).....	96.6

Chromium Oxid Green, Contract No. 8126:

Specific gravity (15.6° C./15.6° C.).....	5.02
Insoluble siliceous matter (per cent.).....	1.7
Ferric oxid (Fe ₂ O ₃) (per cent.).....	0.1
Chromium oxid (Cr ₂ O ₃) (per cent.).....	98.3

Chrome Yellow, Contract No. 8127:

Specific gravity (15.6° C./15.6° C.).....	5.75
Loss at 110° C. (per cent.).....	0.3
Total lead as PbO (per cent.).....	69.5
Chromic anhydrid (CrO ₃) (per cent.).....	28.8
Sulfuric anhydrid (SO ₃) (per cent.).....	0.7
Sodium oxid (Na ₂ O) (per cent.).....	0.3

Zinc Yellow, Contract No. 8125:

Specific gravity (15.6° C./15.6° C.).....	3.50
Loss at 110° C. (per cent.).....	0.2
Total loss on ignition (per cent.).....	13.8
Insoluble in acetic acid (BaCrO ₄) (per cent.).....	1.6
Potassium oxid (K ₂ O) (per cent.).....	10.2
Zinc oxid (ZnO) (per cent.).....	38.2
Chromic anhydrid (CrO ₃) (per cent.).....	41.6
Sulfuric anhydrid (SO ₃) (per cent.).....	2.5

Red Lead, Contract No. 10368:

Specific gravity (15.6° C./15.6° C.).....	8.63
Insoluble in HCl (per cent.).....	0.3
Total lead (Pb) (per cent.).....	91.4
Lead peroxid (PbO ₂) (per cent.).....	23.7

Kaolin, Contract No. 10357:

Specific gravity (15.6° C./15.6° C.).....	2.41
Silica (SiO ₂) (per cent.).....	30.3
Alumina and Oxid of Iron (Al ₂ O ₃ + Fe ₂ O ₃) (per cent.).....	18.6
Lime (CaO) (per cent.).....	15.9
Sulfuric anhydrid (SO ₃) (per cent.).....	21.7
Moisture and undetermined, by difference (per cent.).....	13.5

Magnetic Black, Contract No. 8066:

Specific gravity (15.6° C./15.6° C.).....	4.42
Loss at 110° C. (per cent.).....	0.6
Total loss on ignition (per cent.).....	5.2
Total iron calculated as Fe ₂ O ₃ (per cent.).....	93.2
Ferrous oxid (FeO) (per cent.).....	29.9
Carbon dioxide (per cent.).....	8.0
Sodium.....	present
Calcium.....	trace

This material is, therefore, not pure Fe₃O₄ but has approximately the following composition:

Magnetic oxid of iron (Fe ₃ O ₄) (per cent.).....	60.4
Ferric oxid (Fe ₂ O ₃) (per cent.).....	18.3
Ferrous carbonate (FeCO ₃) (per cent.).....	18.0
Sodium carbonate (Na ₂ CO ₃) (per cent.).....	2.8
Moisture (per cent.).....	0.5

American Vermilion (Scarlet Lead Chromate), Contract No. 10518:

Specific gravity (15.6° C./15.6° C.).....	6.79
Total lead as PbO (per cent.).....	80.9
Chromic anhydrid (CrO ₃) (per cent.).....	17.2
Sulfuric anhydrid (SO ₃) (per cent.).....	1.1
Loss on ignition (below red heat) (per cent.).....	0.8

Linseed Oil, Contract No. 8067:

Color.....	golden brown
Odor.....	normal
Specific gravity (15.6° C./15.6° C.).....	0.9335
Acid number.....	1.7
Saponification number.....	193.6
Iodin number.....	179.6
Ash (per cent.).....	0.15

cluding protective coatings, were transferred from the Geological Survey to the Bureau of Standards, so that the present investigation was conducted under the joint

¹ Results of cooperative investigations carried on by the Bureau of Chemistry and the Bureau of Standards. Presented at the 48th Meeting of the American Chemical Society, Rochester, September 8-12, 1913.

² Chief, Contracts Laboratory, Bureau of Chemistry.

³ Engineer Chemist, Bureau of Standards, Department of Commerce.

been made on most of the phases of this general problem, but, owing to the difficulty of controlling the factors with sufficient exactness to obtain truly comparable results, the progress has been slow.

One of the national technical societies is engaged in this general research, but as no definite information was available on the protection of structural steel subject to intermittent immersion, in the present

investigation the effect of fresh water immersion was studied. Fifteen paints were tested in this series, including twelve standard single pigments, two mixed pigments, and one experimental pigment. As the test was confined to a comparison of pigments the same oil and drier were used throughout the test. All the pigments except the experimental one were standard commercial products purchased in the open market, and analyzed in the usual manner in the Contracts Laboratory, Bureau of Chemistry.

While those tested do not include all the paint materials recommended for the protection of steel structures, they do include the standard types used for this purpose and these tests should be considered as only preliminary to aid in developing a more extended investigation at some later date.

PREPARATION OF DRIER

The drier was made in the laboratory by saponifying with caustic alkali the linseed oil used in the test, dissolving the resulting soap in water and precipitating the lead and manganese linoleates by adding lead acetate and manganous sulfate, respectively. The washed and dried lead and manganese linoleates were dissolved in pure spirits of turpentine so that the resulting solution contained 3.92 per cent lead and 0.79 per cent manganese.

PREPARATION OF PAINTS

Preliminary tests were made with the selected pigments to determine the amount of oil necessary to give a paint of a viscosity, as determined by the Stormer viscosimeter, of about 50 seconds (a paint of this viscosity having been found to have a good consistency for spreading) and to determine the amount of drier to cause the paint to dry in about twelve hours. In the actual preparation of the paints the pigments were ground in an improved No. 2 Harris mill with sufficient oil to form a paste. The pastes were then reground with the remaining oil as calculated from the preliminary tests, the drier was added, and the whole paint again run through the mill. Table I shows the actual composition and viscosities of the finished paints. The specific gravity of each paint was determined by the weight of 100 cc. at 21.1° C. (70° F.).

METAL USED

Plates of basic open hearth steel, one-eighth inch thick, 24 inches long, and 18 inches wide were used for all tests. Analysis of a sample taken from one of the plates gave the following results:

STEEL, CONTRACT NO. 15576

Determination	Bureau of Chemistry Per cent	Bureau of Standards Per cent
Silicon (Si)	0.019	0.019
Sulfur (S)	0.062	0.062
Phosphorus (P)	0.009	0.011
Manganese (Mn)	0.39	0.39
Carbon (C)	0.13	0.11
Copper (Cu)	0.011	0.013

MARKING PLATES

Each plate was marked by the position of one-eighth inch holes drilled 1 centimeter from the long upper

edge of the plate. The distance in centimeters of each hole from the left hand short edge was the same as the number of the paint. As each paint was tested in triplicate, individual plates in each set were distinguished by one, two, or three one-eighth inch holes drilled 1 centimeter from the left-hand short edge and about 20 centimeters down that edge from the upper left-hand corner of the plate (see Fig. 1).

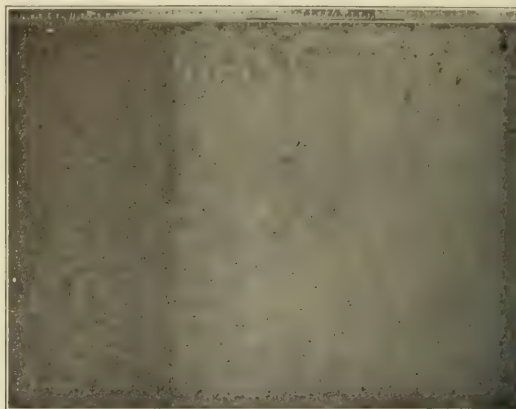


FIG. 1—MARKING PLATES (PAINT NO. 5, SET 1)

CLEANING PLATES

Any method of pickling to clean metal for paint tests is open to the objection that it is exceedingly difficult to insure complete removal of all the acid or salts from the pickled surface. Sand blasting is by far the best method; no corrosive acids are brought into contact with the metal and the sand-blasted surface is an ideal one for the application of paint.

The plates were thoroughly cleansed from all mill scale, dust, grease, etc., by sand blasting until a uniform surface of clean metal was exposed, and were painted while still bright. All were in perfect condition when painted except two, Plate 3 of Paint 1 and Plate 3 of Paint 5, which were somewhat rusted in tiny, deep spots extending rather uniformly over the surfaces. Since there was no appreciable difference between the three plates on these two tests it is evident that these small rust spots had no marked influence.

SPREADING RATE

It was intended to apply all paints at a uniform spreading rate of 900 square feet per gallon. The specific gravities were determined by weighing 100 cc. of the well mixed paint at 21.1° C. (70° F.). (The specific gravity multiplied by 3785.4 gives the weight in grams per gallon, and the product divided by 900 gives the number of grams of paint to be applied to each square foot.) Owing to the difficulty of thoroughly mixing the paints, the specific-gravity determinations are not always correct, and it would probably have been better to have made the calculations from the determined values for the various ingredients of each paint. As some errors were made in calculating, from the determined specific gravities, the weights of

paint to be applied, the spreading rates were not all exactly 900 square feet to the gallon. They do not, however, differ very greatly from this figure and in Table I the spreading rates, calculated from the weight used and the determined specific gravities, are given in column 9, and from the calculated specific gravities, in column 10.

BRUSHES USED IN PAINTING

The brushes used in all the painting in this series of tests were flat chisel-edge flowing varnish brushes of good quality, the length of bristles outside of ferrule being between $2\frac{1}{4}$ and $2\frac{1}{2}$ inches. A new brush was used for each paint and after use it was cleaned in turpentine, then in benzine, allowed to dry, and kept free from dust until used again for a subsequent coat of the same paint.

APPLICATION OF PAINT

Each cleaned plate was supported over a table by four wooden pins which held it at points one-half inch from the edges (see Fig. 2). A suitable quantity of the well mixed paint in a casserole with the brush was weighed on a balance accurate to 10 mg. The paint was applied to the full surface of the plate, brushing backward and forward, and the casserole, paint, and brush were weighed from time to time until the

Any abrasions were retouched, and allowed to dry thoroughly before applying the next coat (see Fig. 3). The second coat was applied to the full width and two-



FIG. 2—METHOD OF SUPPORTING PLATE FOR PAINTING

thirds of the length of the plate and the third coat to the full width and one-third of the length. All tests were conducted in triplicate and by the method of

TABLE I—DATA ON COMPOSITION AND PROPERTIES OF PAINTS USED IN TESTS OF PAINTS FOR STEEL

Paint No.	COMPOSITION OF PAINT	Specific gravity		Viscosity (water = 6.2)	Paint applied per sq. ft. Grams	Weight per gallon (Sp. gr. \times 3785.4)		Spreading rate (sq. ft. per gal.) calculated from		Date of painting		
		Determined	Calculated			From determined sp. gr. Grams	From calculated sp. gr. Grams	6 and 7	6 and 8	Coat 1	Coat 2	Coat 3
1(a)	2270 grams white lead, 947 cc. linseed oil, 30 cc. drier.....	2.45	2.39	53	10.32	9274.2	9047.1	899	877	1910 Aug. 1	1910 Aug. 29	1910 Sept. 16
2	1435 grams zinc white, 2400 cc. linseed oil, 40 cc. drier.....	1.35	1.37	48	5.69	5110.3	5186.0	898	911	"	"	"
3	646 grams white lead, 556 grams zinc white, 825 cc. linseed oil, 40 cc. drier.....	1.78	1.87	46	7.47	6738.0	7078.7	902	948	"	"	"
4	235 grams lampblack, 1300 cc. linseed oil, 40 cc. drier.....	1.00	1.08	47	4.20	3785.4	4088.2	901	973	"	"	"
5(a)	1075 grams special slag pigment, 650 cc. linseed oil, no drier.....	1.83	1.76	46	7.33	6927.3	6662.3	945	903	"	"	"
6	780 grams flake graphite, 1300 cc. linseed oil, 40 cc. drier.....	1.18	1.20	48	4.95	4466.8	4542.5	903	918	Aug. 2	"	"
7	762 grams artificial graphite, 1150 cc. linseed oil, 45 cc. drier.....	1.21	1.21	47	5.07	4580.3	4580.3	903	903	"	"	"
8	1024 grams Indian red, 482 grams kaolin, 1300 cc. linseed oil, 40 cc. drier.....	1.60	1.59	50	6.71	6056.6	6018.8	903	897	"	Aug. 30	"
9	1799 grams Indian red, 1900 cc. linseed oil, 30 cc. drier.....	1.57	1.58	48	6.60	5943.1	5980.9	900	906	"	"	"
10(b)	1764 grams chromium oxid green, 1800 cc. linseed oil, 35 cc. drier.....	1.63	1.59	48	6.88	6170.2	6018.8	897	875	Aug. 3	"	"
11	1400 grams chrome yellow, 2960 cc. linseed oil, 40 cc. drier.....	1.21	1.26	49	5.07	4580.3	4769.6	903	941	"	"	"
12	1230 grams zinc yellow, 1600 cc. linseed oil, 35 cc. drier.....	1.36	1.39	48	5.74	5148.1	5261.7	897	917	"	"	"
13	1553 grams magnetic oxid black, 1950 cc. linseed oil, 40 cc. drier.....	1.48	1.44	50	6.22	5602.4	5451.0	901	876	"	"	"
14	500 grams red lead, 220 cc. linseed oil, no drier.....	2.39	2.54	50	10.04	9047.1	9614.9	901	958	Aug. 4	Aug. 15	Aug. 30
15	900 grams American vermilion, 300 cc. linseed oil, no drier.....	2.88	2.72	50	12.10	10902.0	10296.3	901	851	Aug. 30	Sept. 16	Oct. 12

(a) Plate 3 somewhat rusted in tiny deep spots over practically whole surface.

(b) Second coat did not dry at all for a long time. Was still sticky when third coat was applied.

decrease in weight showed that the required amount of paint had been applied. The plates were then lifted by the edges, turned over, and after the other sides were painted in a similar manner, were placed in a rack where they were supported by four points.

painting each plate represented first, second, and third coat work.

PRECAUTIONS BEFORE EXPOSING PLATES

The preparation of the paints and the painting were done in a room free from laboratory fumes. The plates

TABLE II.—INSPECTION OF TESTS OF PAINTS FOR STEEL. Inspected by Walker and Schmidt, March 1, 1911. All plates in good condition

Paint No.	Inspection by P. H. Walker and G. C. Schmidt, May 1, 1911	Inspection by S. S. Voorhees and P. H. Walker, July 3, 1911	Inspection by S. S. Voorhees and P. H. Walker, August 3, 1911	Inspection by P. H. Walker and G. C. Schmidt, Sept. 5, 1911	Inspection by F. W. Smither and G. C. Schmidt, October 13, 1911	Inspection by P. H. Walker and G. C. Schmidt, December 2, 1911	Inspection by S. S. Voorhees and P. H. Walker, March 1, 1912
1	Good condition.	Good condition; some rust near edges and in few small spots; no apparent difference between coats or different plates.	Plate 1, serious rusting of small area around abrasion(?) on bottom of coat 1; slight rusting on bottom of coats 2 and 3. Plate 2, slight rusting near bottom of coat 1; coats 2 and 3 in good condition. Plate 3, like Plate 2, except much more pronounced rusting on side next to wood of frame. (Plates shifted so as not to touch wood.)	Serious rusting on coat 1, Plates 1 and 2; otherwise like last inspection.	No material change since last inspection.	Considerable rusting. Plate 3 worse than other 2 plates.	Serious rusting through on all coats. Most marked on coat 1. Should have been repainted before.
2	Plate 1 somewhat blistered at bottom of coats 2 and 3; Plates 2 and 3 in good condition. Good protection.	Good; some rust on coat 1; most pronounced on Plate 1 which also shows some blisters at lower edge of coat 3.	All show slight rusting on coat 1. No rust on coats 2 and 3. On Plate 2, coat 3, bright metal observed under loose blister $\frac{1}{4}$ in. in diameter.	Little change since last inspection.	Slight blistering on coat 2, decided blistering on coat 3. Bright metal under blisters.	Some rust showing; more pronounced on Plate 1. Blisters more pronounced than on last inspection.	Serious corrosion on lower part of plates. Blistering on coat 1 and 2 with bright metal underneath. Paint has lost life on coats 1 and 2. Should have been repainted before.
3	Plate 1 considerably blistered at bottom of coats 2 and 3. Some blistering on Plates 2 and 3. Good protection.	Good; some rust showing on coat 1. Most pronounced on Plate 1 which shows blisters at lower edge of coat 3.	Same as Paint 2, except bright metal observed under blisters on all plates.	Little change since last inspection.	No material change since last inspection.	Decided blistering on coat 3, Plates 2 and 3; slight blisters on coat 2, Plate 2; otherwise like last inspection.	Very slight rusting in body of paint; slight blistering with bright metal underneath, especially on coat 3. Needs repainting.
4	Plate 1 slightly blistered; Plates 2 and 3 good; good protection.	Good; some rust on coat 1, Plate 1; very little on Plates 2 and 3.	No rust observed on any of the plates, but peculiar white spots were observed (growth of some kind).	Some rust on coat 1, Plate 1; otherwise like last inspection.	Little change since last inspection.	Decided rust on coat 3, Plate 3 being worse than other two. Some rust on coats 1 and 2, but not so pronounced as on coat 3.	Breaking through in fine rust spots, which have spread on surface. Needs repainting but is better than Paint 3.
5	Some rust on all 3 plates.	Coat 1, rusting all over on all 3 plates. Considerable rust on coats 2 and 3. Plate 3, very little rust.	Coat 1 very badly rusted. Coat 2 considerable rust. Coat 3, some rust. Paint failing.	All 3 plates need repainting; removed from tank and exposed on roof.	More rust on coat 1. Otherwise like last inspection.	Considerable rust on coat 3 and some on Plates 1 and 2, but wise like last inspection.	Some breaking through on all coats. Plates 1 and 2, but not so much as Paint 4. Needs repainting.
6	Slight rust on coat 1, Plate 1. Plates 2 and 3 in good condition.	Coat 1, peeling on all 3 plates; coats 2 and 3 in good condition.	Coat 1 slightly rusted. Coats 2 and 3 practically perfect.	More rust on coat 1. Otherwise like last inspection.	About same as last inspection.	Considerable rust on coat 3 and some on Plates 1 and 2, but wise like last inspection.	Some breaking through on all coats. Plates 1 and 2, but not so much as Paint 4. Needs repainting.

7	Good condition except some scratched places.	No change since last inspection.	Good condition.	Coat 1 slightly rusted. Coats 2 and 3 practically perfect.	Same as last inspection.	About same as last inspection.	Some rust on coat 3, Plate 1; more pronounced on Plate 2; practically none on Plate 3.	Similar to Paint 6 but perhaps slightly more corroded. Needs repainting.
8	Good condition except some scratched places.	No change since last inspection.	Very slight rusting on coat 1. Good condition.	Possible indication of very slight corrosion on coat 1. Coats 2 and 3 perfect.	Same as last inspection.	Coat 1 same as last inspection. Coat 2, Plates 2 and 3 show indication of rust. Coat 3, more rust.	Same as last inspection.	Coat 1 badly corroded. Coats 2 and 3 breaking through worse than Paints 6 and 7. Needs repainting.
9	Practically perfect.	Practically perfect.	Good condition.	Possible indication of very slight corrosion on coat 1. Coats 2 and 3 practically perfect; corrosion on coat 1 less than in Paint 8.	More corrosion on coat 1 than in Paint 8. Otherwise like last inspection.	About same as last inspection.	About same as last inspection.	Similar to Paint 8. Needs repainting.
10	Little rust on coat 1. Plates 1 and 2. Plate 3 good.	Plate 1, rust on coats 2 and 3. Plate 2, a little rust on coat 1. Plate 3 good.	Coat 1, decided rusting on 3 plates.	Considerable rusting over whole of coat 1. Few spots of rust on coat 2. Coat 3 good.	Same as last inspection.	About same as last inspection.	Same as last inspection.	Coat 1 breaking through badly. Coats 2 and 3 in fair condition. These probably do not need repainting.
11	Good condition except one or two scratches.	No change since last inspection.	Coat 1, some rust; most pronounced on Plate 2.	Some rust on coat 1. No rust on coats 2 and 3.	Coat 1 badly rusted on Plates 1 and 2; slightly rusted on Plate 3. Coats 2 and 3, no change.	About same as last inspection.	Coat 1 considerably rusted; most pronounced on Plate 1; least on Plate 3.	Similar to Paint 10, except that coat 3, Plate 2, is breaking through.
12	Good condition except one or two scratches.	Plates 1 and 2 in good condition except one or two scratches. Plate 3 a little rust on coat 1.	Good condition.	Somewhat less rust on coat 1 than on Paint 11. No rust on coats 2 and 3.	Some rust on coat 1 on all plates, coats 2 and 3 good.	About same as last inspection.	Same as last inspection.	Best plates yet; some breaking through on coat 1, coats 2 and 3 in good condition. Do not need repainting.
13	Good condition.	A little rust on coat 1, on all plates.	Coat 1 failed. Coats 2 and 3 in good condition.	Coat 1 badly rusted. Coats 2 and 3 in good condition.	Coats 2 and 3 show some rust; most pronounced on Plate 3.	Coat 1 badly rusted. Coats 2 and 3 about same as last inspection.	Coat 1 considerably rusted; some rust on coat 2.	Coat 1 badly corroded, coat 2 somewhat corroded, coat 3 in good condition. Coats 1 and 2 need repainting.
14	Practically perfect.	Practically perfect.	Practically perfect.	Perfect, best yet.	Perfect.	Perfect.	Practically perfect.	Coat 1 gives fair protection, slight corrosion, coats 2 and 3 in excellent condition; best so far.
15	Practically perfect.	Practically perfect.	Excellent. A few spots on coats 1 and 2 of Plates 1 and 2, apparently abrasions.	Practically perfect. Equal to Paint 14.	Perfect.	Perfect.	Practically perfect. Peculiar growth, most pronounced on coat 3, Plate 2.	On coat 3, Plates 2 and 3, some discoloration which may be under paint. In other respects like Paint 14.

were dried in this room and kept there until the exposure tests were begun.

EXPOSURE OF PLATES

Three rectangular tanks large enough to hold 25 plates 18 by 24 inches were used for the exposure test. Tanks 1 and 2 were of wood and unlined, and tank 3 was lined with sheet lead. It was soon found, however, that tank 1 leaked so badly that it was necessary to line it. This was done with sheet zinc, so the



FIG. 3.—FRAME FOR DRYING PLATES

actual exposures were made in a zinc-lined tank, an unlined wooden tank and a lead-lined tank. The plates were held in a vertical position by a wooden framework so that they were in contact with wood only and were separated from one another by a space of about 1 inch.

The tests proper were started on February 1, 1911, when one plate of each test was placed in each of the tanks mentioned, these tanks being filled with water every afternoon at 4 o'clock and emptied the next morning at 9 o'clock. This filling and emptying was done each working day, except when the water was frozen from February 21 to 23, on March 16, and December 28, 1911, and from January 5 to 22, 1912. On the last named date the plugs were removed from the tanks and the water allowed to drain off as soon as the ice melted. The plates were kept in the empty tanks from that time. Table I gives data on the composition and properties of the paints used, spreading rates, dates of painting, and notes made while applying the paints; Table II gives results of nine inspections of these tests.

DISCUSSION OF FORMULAS USED

Paints 1, 2, 3, and 4 are standard formulas and

require no comment. Paint 5, special slag pigment, is not a commercial pigment but is a material furnished by the Office of Public Roads, United States Department of Agriculture, as a material which, owing to its rust-inhibiting properties in aqueous solution, might be of service as a pigment. The analysis, however, shows the material to be highly basic in character and it was obviously impossible for it to produce a durable paint with linseed oil.

Paints 6 and 7 require no comment.

Paint 8, Indian red and kaolin, was intended to approximate in composition some of the native iron oxid pigments and at first China clay was secured to dilute the Indian red, but this was rejected since it was found to be largely adulterated with calcium sulfate. Kaolin, passing the United States Pharmacopoeia tests, was then used and the paint made and applied, but on making the analysis later this kaolin also was found to contain a large amount of calcium sulfate. An examination of the tests for kaolin in the Pharmacopoeia shows that these tests will not secure pure kaolin; the tests for this material should be thoroughly revised in the next edition of the Pharmacopoeia.

Paint 9 requires no comment.

Paint 10 is a little used and expensive pigment, but as its color is probably more permanent than that of any green made by mixing blue and yellow and as it has been used with good results in painting the cages at the National Zoological Park, Washington, D. C., it was deemed advisable to include it in the tests. The very peculiar behavior of this paint on drying is worthy of note. The first coat dried in less than twelve hours, but the second coat was not even tacky at the end of several days and was exactly like a mixture of pigment in a non-drying oil. It was at first thought that either some mistake had been made in the paint or that some unusual weather condition caused this peculiarity, but on painting a fresh piece of steel with the same paint, it was found to dry well as a first coat, but failed to dry as a second coat. The authors have no explanation to offer of this phenomenon.

Paint 11 requires no comment.

Paint 12, zinc yellow, is an expensive pigment, but has been highly recommended by some authorities as an inhibitor of rust.

Paint 13, magnetic oxid black, is a comparatively new pigment. It is worthy of note that the analysis shows the material not to be pure Fe_3O_4 .

Paint 14 requires no comment.

Paint 15, American vermilion or scarlet lead chromate, is an expensive pigment, but one which from its excellent record in other tests should be included in any set of pigment tests.

CONCLUSIONS

The results of inspections given in Table II require very little comment. There are some inconsistencies in the reports, but as these inspections are merely results of general opinions on the condition of the plates inspected, such inconsistencies are to be expected. The notes are given essentially as taken down by the inspectors at the time of inspection.

The authors realize that no sweeping conclusions can be drawn from any one series of tests, and while they feel that more care has been taken to eliminate all variables except the pigments than has been taken in any previously published service tests, they think that results which are not in accordance with previous tests and experience should be taken with caution. The excellent showing, however, of Paints 14 and 15 are wholly in accordance with investigations by others and with the experience of users of paint for steel. Red lead and linseed oil and American vermilion (scarlet lead chromate) and linseed oil are undoubtedly among the very best for the protection of iron. The suggestion is therefore offered that future tests be made by adopting such a formula as Paint 14 as a standard and painting half of each plate tested with the standard and the other half with the paint to be tested. If the plates are cleaned by sand blasting instead of pickling it can safely be assumed that the only variable is the paint and much better conclusions may be drawn than when possible variations in the metal must also be considered.

BUREAU OF CHEMISTRY AND BUREAU OF STANDARDS
WASHINGTON

THE CORROSION OF METALS BY WATER

By A. T. STUART

Received June 17, 1913

PART I—RELATIVE CORROSIVITY OF "MECHANICALLY FILTERED" AND "RAW" WATER

Conditions in each of the following series of experiments were quite uniform so that comparisons within that set are possible. The metals used were employed in the form of wires, cut in equal lengths. These were coiled and suspended in bottles containing 400 cc. of the water to be examined. The measure of corrosion was obtained by wiping the wires with a cloth and finding the loss in weight.

In order to ascertain the effect on corrosion of unlike metals in contact, two common metals of greatest difference in potential were chosen. The wires were wound around each other, then coiled and suspended as before.

These tests were not allowed to last longer than seven days, for it was felt that in that time actual conditions in any civic supply were already exaggerated, contact surfaces considered. At the end of that time considerably larger amounts of iron were capable of being transported by the water than could ever be tolerated in practice.

The following waters were tested:

1. From Watertown, N. Y., "mechanically filtered," Sample "A."
2. From Watertown, N. Y., "mechanically filtered," Sample "B."
3. From Watertown, N. Y., "raw," Sample "C."
4. From Ottawa, Ont., "mechanically filtered," Sample "D."
5. From Ottawa, Ont., "raw," Sample "E."
6. From Ottawa, Ont., "chlorinated" (only), Sample "F."
7. From Ottawa, Ont., MgO used as precipitant, Sample "G."

Experiment 1A showed that waters "A," "B," and "C" were equally corrosive.

It is evident from these figures that no appreciable differences exist in the action on iron of raw or treated waters (mechanical filtration) in so far as they may be revealed by losses in weight of the metals. It is sig-

nificant that the results obtained are the same for all samples of water except sample "G."

Although these figures are practically identical, there are extreme and important differences in the character of the water. Thus, it was found that raw

LOSSES IN WEIGHT (GRAMS) OF VARIOUS METALS DUE TO CORROSION BY

Water	WATER					
	Exp. 1—Iron Wire "A" Alone		"A"		"B"	
At 22° C.	0.0269	0.0274	0.0280	0.0284	0.0282	0.0271
At 50° C.	0.0394	0.0317	0.0324	0.0316	0.0300	0.0258

Water	Exp. 2—Iron Wire "A" Alone		
	"E"	"D"	"G"
At 22° C.	0.0277	0.0261	0.0203
At 50° C.	0.0540	0.0529	0.0185

Iron and copper	Water "E"		Water "D"	
	Iron	Copper	Iron	Copper
At 22° C.	0.0369	0.0000	0.0375	0.0000
At 50° C.	0.0743	0.0000	0.0592	0.0000

Iron and aluminum	Iron		Aluminum	
	Iron	Aluminum	Iron	Aluminum
At 22° C.	0.0248	0.0000	0.0225	0.0000
At 50° C.	0.0315	0.0023	0.0260	0.0028

Iron alone	Iron		Iron	
	Iron	Aluminum	Iron	Aluminum
At 22° C.	0.0317	0.0328	0.0328	0.0000
At 50° C.	0.0317	0.0328	0.0328	0.0000

Lead & aluminum	Lead		Aluminum	
	Lead	Aluminum	Lead	Aluminum
At 22° C.	0.0016	0.0003	0.0067(?)	0.0000
At 50° C.	0.0023	0.0003	0.0013	0.0014

Lead alone	Lead		Lead	
	Lead	Aluminum	Lead	Aluminum
At 22° C.	0.0012	0.0007	0.0007	0.0000
At 50° C.	0.0011	0.0014	0.0014	0.0000

(Water "F" used in All Cases. Iron Wire "B")

Iron alone	At 22° C.		At 50° C.	
	Iron	Copper	Iron	Copper
Iron.....	0.0289	0.0292	0.0589	0.0578

Iron & aluminum	At 22° C.		At 50° C.	
	Iron	Aluminum	Iron	Aluminum
Iron.....	0.0220	0.0211	0.0125	0.0168
Aluminum.....	0.0000	0.0000	0.0034	0.0026

Iron & copper	At 22° C.		At 50° C.	
	Iron	Copper	Iron	Copper
Iron.....	0.0318	0.0314	0.0623	0.0603
Copper.....	0.0000	0.0000	0.0000	0.0000

Lead alone	At 22° C.		At 50° C.	
	Lead	Aluminum	Lead	Aluminum
Lead.....	0.0016	0.0020	0.0045	0.0034

Lead & aluminum	At 22° C.		At 50° C.	
	Lead	Aluminum	Lead	Aluminum
Lead.....	0.0014	0.0031	0.0032	0.0032
Aluminum.....	0.0005	0.0000	0.0010	0.0004

Lead & copper	At 22° C.		At 50° C.	
	Lead	Copper	Lead	Copper
Lead.....	0.0336	0.0436	0.1203	0.1192
Copper.....	0.0000	0.0000	0.0000	0.0000

Copper & aluminum	At 22° C.		At 50° C.	
	Copper	Aluminum	Copper	Aluminum
Copper.....	0.0000	0.0000	0.0000	0.0000
Aluminum.....	0.0084	0.0089	0.0036	0.0035

waters, although corroding iron to the same extent, do not coat the iron with as much flocculent material nor do they allow it to settle out, as is the case with treated waters, but retain a large proportion in solution, which may perhaps be of a colloidal nature. Treated waters, at ordinary temperatures, became very murky and opaque and, when hot, large amounts of brownish red rust appeared. This is popularly known as the "red water trouble." However, it must be noted that our figures indicate that the actual amounts of iron corroded were the same for treated or raw waters.

PART II—EFFECT OF WATER ON METALS IN CONTACT Apparently the state assumed by the iron corroded from the metal is a much more important question from the standpoint of a city supply than the actual amounts. The conclusion in this connection is that

the so-called mechanical treatment of waters of these types is very liable to bring about this troublesome discoloration.

It may be noted here that both these waters examined were of low mineral content and highly colored by peaty matter. It would be of interest to follow this matter further with various other types.

These figures are in excellent accord with the electrolytic theory of corrosion and illustrate an easy means for investigating this subject. A graphic representation could be presented with the aid of further figures which would be very interesting.

CHEMICAL LABORATORY, DEPARTMENT OF AGRICULTURE
EXPERIMENTAL FARM, OTTAWA, ONT.

SOME EXPERIMENTS ON THE CONVERSION OF LONG-LEAF PINE TO PAPER PULP BY THE SODA AND SULFATE PROCESSES¹

By SIDNEY D. WELLS

INTRODUCTION

During 1912 the Forest Service in coöperation with the University of Wisconsin undertook a series of experiments on longleaf pine, *Pinus palustris*, with the following objects:

1. To study what influence the variable cooking conditions have in the sulfate process of pulp-making.
2. To determine the suitability of longleaf pine for paper pulp.
3. To compare the sulfate process with the soda process.

This work has been only partially completed but since there is urgent demand for information on the adaptability of longleaf pine, or southern pine as it is more commonly called, for the manufacture of paper pulp, it has been thought advisable to give what indications our work has so far made manifest.

Longleaf pine was chosen on account of the large quantities of this wood that are being wasted in the lumber operations of the southern states and also because many logs are at present being sawed into lumber at little or no profit on account of their small diameter which would be of admirable size for pulpwood. Furthermore, the large amount of resinous matter in this wood made it desirable as an extreme test of a cooking process and the long, thick-walled fibers of the wood assured a strong pulp if it could be produced without a too drastic treatment.

EXPERIMENTAL PROCEDURE

The cooking operations in this work were conducted in two forms of digesters. The first form consisted of a small rotary autoclave of about 2-gallon capacity which was heated with Bunsen burners. The other form was a vertical digester of 60-gallon capacity, heated by direct steam. The greater portion of the work was accomplished in the former and in all 145 cooks made. The data obtained in these cooks were used in determining the conditions for the larger digester in which 19 cooks were made to obtain conditions more nearly comparable with those used in commercial practice.

¹ Paper presented at the 48th Meeting of the A. C. S., Rochester, September 8-14, 1913.

The wood used was procured in Louisiana and Mississippi, and was fairly average in rate of growth, size, and content of resinous matter. It was freed from bark and reduced to chips five-eighths of an inch long with the grain. These chips were allowed to become air-dry and were thoroughly mixed and sifted to remove any dirt and small pieces.

The cooking liquors were made up by dissolving the required amounts of commercial caustic soda, sodium sulfide, Glauber's salt, and soda ash to produce solutions of the desired concentration of each of these chemicals.

In studying the influence of the variable factors entering into the cooking operation the small autoclave was used. The effect that any one variable condition exerted was determined by a series of cooks made varying the condition under observation, and maintaining the other conditions as nearly identical as possible in each cook. The effects were ascertained by determining the yield of pulp and carefully treating the pulp in a hollander beating engine to develop a stuff capable of producing as strong a sheet as possible when made into paper. The quality and color of the pulps were judged by inspection, feel, amount of beater treatment necessary, and the strength and wearing qualities of the paper produced.

THE EFFECTS OF VARYING THE AMOUNTS OF CHEMICALS

The effect of varying the caustic soda or sodium sulfide was a decrease in yield and a lighter colored pulp with an increase in either one or both of the chemicals. Caustic soda was found to be about twice as drastic in its action as sodium sulfide and with the same yield the pulp produced by the former was lighter than that produced by the latter. The yields, however, do not decrease directly in proportion to the amounts of chemical used, and between 30 and 50 pounds of caustic per 100 pounds of chips the decrease in yield is much less for equal steps than below or above these amounts. The disagreeable odor caused by the production of mercaptans increased with the increase of the sodium sulfide, and was much more noticeable where the larger proportions of this chemical were used.

The sodium carbonate and sulfate present in the cooking liquor produced no very apparent effect except where the former was present in relatively large amounts when a retardation in the action of the other chemicals present was noticeable. Enough cooks were not made, however, to definitely establish this indication.

THE EFFECT OF VARYING THE PRESSURE, DURATION OF COOKING AND CONCENTRATIONS

The effect of increasing any one of these variables was to increase the severity of the cooking action attainable with the same quantity of cooking chemicals. With any combination of the above conditions there is a definite amount of chemical necessary to produce a pulp of the best quality and it is possible to use a wide range of conditions to produce approximately the same result.

SEMI-COMMERCIAL COOKS

In the cooks in the large digester the object sought was to obtain the best quality of pulp. It was found that easily-bleaching pulps could not be obtained without using a very drastic digestion with a high percentage of alkali, and that the pulps produced were very low in yield and extremely soft and weak. It was, therefore, decided to devote attention toward producing the strongest pulps possible, and treat these pulps in the beater to make the highest grade of "Kraft." Although the strength of the paper was constantly considered, the question of yield was also very important and the best cooks were determined with these two objects in view.

The best cooks secured were made under the following conditions:

Caustic soda charged per 100 pounds bone dry chips, pounds.....	15.0
Sodium sulfide charged per 100 pounds bone-dry chips, pounds.....	7.5
Initial concentration caustic soda in cooking liquor, grams per liter.....	26.5
Initial volume liquor per pound of chips, gallon.....	0.68
Total duration of cook, hours.....	3.5
Duration of cook at maximum steam pressure, hours.....	3.0
Maximum steam pressure, pounds per square inch.....	100.0

The yields of crude pulp under these conditions were 49 per cent of the weight of the wood and the

with these pulps using the same or an even less consumption of power and in much less time.

SODA COOKS

To compare the soda process with the sulfate process in cooking longleaf pine several soda cooks were made. It was found that soda pulps could be made that would produce paper capable of resisting bursting pressure to the same degree as the best paper made from sulfate pulp but the wearing qualities were not nearly as good and the yields were from 5 to 10 per cent less. The unbeaten pulps were soft and fluffy for even slightly undercooked pulps, and although they could be hardened in the beater the treatment was longer, and much greater care had to be exercised to avoid cutting the fibers. Furthermore, although a fairly good grade of kraft can be made of sulfate pulp with a yield of 60 per cent, soda pulp produced with that yield would be so undercooked and brittle that only very poor wrapping could be produced. Moreover, it was found necessary to cook soda pulp at least 6 hours to secure good results while in the sulfate process $3\frac{1}{2}$ hours were found sufficient. Thus in the latter process the same digester capacity would produce two-thirds more pulp per day.

COOKING CONDITIONS FOR FOUR TYPICAL SEMI-COMMERCIAL COOKS

	Caustic soda charged per 100 lbs. bone-dry chips	Sodium sulfide charged per 100 lbs. bone-dry chips	Initial concentration of caustic soda in cooking liquor	Initial volume of cooking liquor per 100 lbs. bone-dry chips	Total duration of cook	Duration at maximum steam pressure	Maximum steam pressure	Yield of crude pulp	Beater treatment			Pop test per 0.001 inch of thickness
									Duration of brush	Period of lowering roll	Duration of stiff brush	
	Lbs.	Lbs.	Grams per liter	Gallons	Hours	Hours	Lbs. per sq. inch	Per cent	Hours	Hours	Hours	Lbs.
Large yield.....	15.0	7.5	26.5	68.0	3.0	2.8	90	61.2	1.5	0.5	2.0	7.0
Medium yield.....	15.0	7.5	26.5	68.0	3.5	3.0	100	49.0	4.0	0.5	2.5	9.0
Small yield.....	20.0	10.0	44.6	54.0	3.0	2.5	103	45.3	1.5	0.5	1.5	10.0
Soda cook.....	30.0	0.0	90.0	40.0	6.0	5.5	100	39.8	6.0	0.0	0.0	9.0

strength of the paper produced as determined on the Mullen tester was 9 pounds per thousandth of an inch of thickness. An average sheet of 0.005 of an inch tested 45 pounds and weighed 45 pounds per ream of 500 sheets 24 inches by 36 inches. Not only was the paper exceptionally strong but it was very resistant to wear and folding. The latter fact is apparent by some tests made on it in a Schopper Folding Tester in which it withstood 1200 double folds before breaking.

The pulps under these conditions were very chippy when blown but the chips were very soft, had no hard hearts and were readily broken up in the beater. An ordinary hollander with steel fly bars was used and the pulp was beaten two hours at light brush, four hours at stiff brush, and one-half hour was spent in lowering the roll from one stage to the other.

Stronger papers than these were produced but the yields fell off considerably. Yields up to 61 per cent were obtained but the strength fell off more than could be compensated by using proportionately heavier paper. It is very probable that with basalt lava beater rolls a stronger paper could have been produced

GENERAL CONCLUSIONS

Although the experiments performed in this investigation are only a portion of what are contemplated they seem to make apparent the following facts:

I. That longleaf pine is well adapted for the manufacture of natural-color kraft pulps and papers.

II. That the sulfate process when applied to this wood affords pulps of better quality and higher yields than the soda process.

III. That kraft paper can be made from longleaf pine equal or superior in quality to the imported or domestic kraft papers now procurable.

IV. The high specific gravity of the wood insures a greater yield per cord to this wood than is possessed by any other commercially important pulpwood.

The data of these experiments given in greater detail is contained in a report entitled "The Utilization of Longleaf Pine for Paper Pulp" by H. E. Surface and R. E. Cooper which is now in press at the Government Printing Office.

INVESTIGATIONS WITH THE U. S. BUREAU OF MINES MODIFICATION OF THE ABEL-PENSKY AND PEN- SKY-MARTENS FLASH-POINT TESTERS¹

BY IRVING C. ALLEN AND A. S. CROSSFIELD

In the handling of lamp oils, particularly in mines and in buildings where open lights are used, it is important that a relatively safe oil, *i. e.*, one with a high flash point, be employed. Equally important is the determination of the inflammability of all oils in common use. This paper, which is a brief of Technical Paper No. 49, published by the Bureau of Mines in the interest of greater safety at mining and metallurgical plants, does not aim to establish definite flash points for oils but describes the instruments and methods of testing that can be used as a basis on which to establish such flash points.

THE FLASH POINT

In the various methods used for determining the flash point of an oil the temperature at which its vapor flashes is not a definite factor but is dependent on a number of physical and chemical conditions not under the control of the operator. It is not an indication of the value of an oil for any particular purpose. It is an indication only of the temperature at which the oil gives off vapors in such proportions that they form an inflammable mixture with the air. If exposed to an electric light or a flame the mixture will ignite and the flame extend throughout the mixture, that is, an explosive mixture of vapor and air is formed.

THE FIRE HAZARD

The flash point, although probably the most important factor, will not, by itself, determine the fire hazard of any substance. The fire hazard of a substance is also affected by the volatility, the boiling point, the vapor pressure, the vapor density, the diffusibility and tendency of the vapors to travel and their explosive limits in air, its tendency to chemical change, the quantity of heat liberated per unit of time and unit of volume, the temperature of the flame, the corrosive action and toxic properties of the substance and of its products of combustion, its behavior toward water both before and after ignition, and the tendency of the substance to leak.

A requirement that an oil has the highest practicable flash point, tending thereby to reduce the fire hazard to a minimum, is praiseworthy and humane. To require too high a flash point may impair the burning qualities of a lamp oil and also work a hardship on the refiner. However, the immediate profits of the refiner should be deemed less important than the safety of the user and the protection of the public against possible loss of life and of property by fire.

The fire hazard of lubricating oils is of importance when the lubricants are used in rapidly running machinery, as in spinning mills, wood mills, etc., or in factories containing combustibles and in compressors for air, ammonia, or other gases.

Particular attention should always be given to the

handling, storage, and inspection of all inflammable liquids.

The Bureau of Mines in Technical Paper No. 49 has recommended the adoption of a modified form of the Abel-Pensky and Pensky-Martens testers for the determinations of the flash points of oils flashing below 150° C. The reasons for the recommendations of these testers are clearly set forth in Technical Paper No. 49, a brief abstract of which includes (1) the reasons for the necessity of exact determination of flash points of oils to determine the fire hazard with their use; (2) the historical development of flash-point testing with descriptions of testers in use; (3) the different factors that influence the obtaining of exact and concordant results; (4) and directions for the use of the two testers recommended.

The modifications of the older forms of Abel-Pensky and Pensky-Martens testers consist of the following: each cup has been fitted with an annular overflow cup into which the excess of oil due to the expansion on heating flows through a small opening in the side of the cup on a level with the filling point. This assures the volume of the oil and the volume of the vapor mixture above the oil remaining constant. The Abel-Pensky tester is provided with a paddle-wheel stirrer identical with that of the Pensky-Martens, while the automatic slide of the Abel-Pensky tester has been fitted to the Pensky-Martens cup. However, in the last change it was found necessary to raise the clock work on posts above the hot bath as the intense heat drew the temper from the spring. The two testers as recommended are identical with the exception of the use of the water bath for the testing of low flash oils and the metal-air bath for those of high flash point. The cups, the automatic opening devices and the stirrers of the two testers are interchangeable. An investigation undertaken in these laboratories indicates that the Pensky-Martens tester can be used very satisfactorily for the testing of low flash-point oils though the temperature regulation is not as nice as with the water-jacketed Abel-Pensky tester. The same conclusion has been reached by other investigations.¹ Each tester is fitted with gas or oil ignition burners.

The present paper includes results of a brief investigation with the two testers. A degree of accuracy greater than 0.5° C. for oils flashing below 100° C. and 1.0° C. for oils flashing above 100° C. was not attempted and any fractions of degrees reported in subsequent tables are derived as averages of several tests or from thermometer, barometer or instrument corrections.

STANDARDIZATION OF INSTRUMENTS

To obtain comparable results the two instruments were compared with an Abel-Pensky tester standardized in 1908 by the Physikalische Technische Reichsanstalt, certificate No. S. & R. 3114. Determinations of flash points of three different oils were made on the three instruments. Results obtained are the averages of five tests agreeing within 0.5° C. and are shown in Table I.

¹ Paper presented at the 48th meeting of the A. C. S., Rochester, September 8-14, 1913, by permission of the Director of the U. S. Bureau of Mines.

¹ Dr. H. Wiebe, "Die Obere Brauchbarkeitsgrenze des Abel-Pensky'schen Apparates und seine Vergleichung mit dem Pensky'schen Flamm-punktprüfer, *Petroleum*, 1913, Band VIII, S. 1061.

TABLE I—COMPARISON OF BUREAU OF MINES TESTERS WITH ABEL-PENSKY
TESTER S. & R. 3114
Average of five tests each

Sample	F. P. by B. of M.		Difference	F. P. by B. of M.		Difference
	Abel- Pensky S. & R. 3114	modifi- cation Abel- Pensky		modifi- cation Pensky- Martens		
X	47.3°	48.0°	+0.7°	49.0°	+1.7°	
No. 1086	36.3°	37.0°	+0.7°	37.8°	+1.5°	
No. 1087	44.5°	45.5°	+1.0°	46.2°	+1.7°	
Average			0.8°			1.6°

In all results hereafter reported the above corrections have been made. The large corrections obtained make it advisable to have all instruments intended for exact work compared with some fixed standard.

USE OF GAS AND OIL IGNITION FLAMES

The use of gas or oil test flames is optional. Comparative tests made, using natural gas, colza oil and lard oil as ignition flames, gave results with a maximum difference of 0.3°, which is well within the error of manipulation. A petroleum distillate, "300° burning oil," on the other hand, gave a flash approximately 0.8° too high and the use of such an oil as an ignition flame is not recommended. The difference is probably accounted for by the fact that the latter flame was quite difficult to regulate, due to its rapid flow through the wick and that the combustion was incomplete as indicated by a bright luminous flame, which in itself may have obscured the first flash. For ease of manipulation a gas flame is most desirable.

TABLE II—COMPARISON OF FLASH POINTS WITH GAS AND OIL TEST FLAMES

Sample	Lard oil Colza oil			Instrument used
	Gas test flame	oil test flame	oil test flame	
1087	45.5	45.4	45.2	B. of M. modification
Kerosine X	48.0	48.1	47.7	of Abel-Pensky

INFLUENCE OF STIRRER

The heat is applied to the oil from the bottom and sides of the cup with the result that there are convection currents set up within the oil with the general direction across the bottom of the cup, up the sides, across the top and down the center and past the thermometer bulb. Consequently, the oil as it passes the

TABLE III—INFLUENCE OF STIRRER
Average of three tests each

Sample	F. P. B. of M. Pensky-Martens stirred		F. P. B. of M. Pensky-Martens unstirred		Flash point Pensky-Martens stirred		Flash point Pensky-Martens unstirred	
	F. P. B. of M. Pensky-Martens stirred	F. P. B. of M. Pensky-Martens unstirred	F. P. B. of M. Pensky-Martens stirred	F. P. B. of M. Pensky-Martens unstirred	Flash point Pensky-Martens stirred	Flash point Pensky-Martens unstirred	Flash point Pensky-Martens stirred	Flash point Pensky-Martens unstirred
Kerosine X	46.2	45.7
1086	37.0	37.1	35.6	35.1
1087	46.2	45.4	45.5	45.2	44.3	45.8
1092	117.0	115.1
1095	184.7	183.0
1096	196.4	195.6

thermometer is slightly cooler than that at the circumference of the surface and a lower flash point will be

recorded than is actually the case. This is clearly shown in Table III. Further, the greater the rate of heating the greater will be the convection currents and consequently the greater will be the difference between the temperature of the oil at the circumference and the temperature at the center of the cup. Also the higher the flash point the greater will be the temperature differences. The differences are almost entirely removed by the use of a stirrer and it has been found easier also to get concordant results in a stirred cup than in one that is without a stirrer.

Different investigators (B. of M. Tech. Paper No. 49, p. 12) have found that a definite filling of the cup has a very appreciable influence on the determination of the flash point. Filling the cup above the point raises the flash point. The reasons for this are quite apparent. The oil as it is heated expands, the surface of the oil is brought nearer the test flame and a lower flash point results. Expansion of the oil reduces the volume of the gas mixture, an explosive mixture is formed at a lower temperature and consequently a lower flash point is recorded. An explosive mixture would be obtained at a lower temperature from a fixed weight of oil than from a fixed volume and a lower flash point would result. To do away with these sources of error the modified testers have been fitted with overflow cups so that as the oil is heated the increase in volume is run off and both volume of oil and volume of vapor mixture are kept constant. The above assumptions are borne out in Table IV.

TABLE IV—COMPARISON OF FLASH POINT WITH CONSTANT WEIGHT AND CONSTANT VOLUME

Sample	Average of three tests		Difference
	F. P. B. of M. modified Pensky-Martens constant vol.	F. P. B. of M. modified Pensky-Martens constant weight	
1087	46.2	45.8	0.4
1092	117.0	115.1	1.9
1095	184.7	183.0	1.7
1096	196.4	195.3	1.3

The suggestion has been made that the overflow oil in the outer cup will be much hotter than the temperature indicated by the thermometer within the cup, that the vapors liberated will pass back into the cup and give a flash below the true flash of the oil, but it is believed that such conditions do not exist. In the first place the cup is so constructed that the bottom is directly exposed to the hot bath and if stirred the oil in the cup is at a temperature not appreciably lower than that in the overflow cup. The volume of the oil that overflows is small compared with that in the cup; and the quantity of vapors liberated from such a small volume even at a slightly higher temperature would have little effect on the flash point, particularly that fraction of the small volume which might pass back into the cup. Also, it is hardly to be assumed that the vapors would pass back into the cup rather than escape around the loose fitting ring of the overflow cup. The views above are borne out by the fact that in no case was the flash point of an oil determined in the cup with the overflow lower than that obtained when the overflow out-

let was plugged. As further proof, comparisons were made of the flash point of an oil obtained in the usual way and of the flash obtained by placing a quantity of low flash oil in the overflow cup. The results are shown in Table V.

TABLE V

Test	Sample No. 1087 with 5 cc. of Sample No. 1086 (F. P. = 37°) in the overflow cup		Instrument used
	Sample No. 1087	Sample No. 1086	
No. 1.	45.4	45.4	B. of M. modified Abel-Pensky
No. 2.	45.3	45.4	
No. 3.	45.8	45.4	
Average.	45.5	45.4	

SUMMARY

The important factors to be considered in the construction and manipulation of an instrument to determine the flash point of an oil may be stated as follows:

- (1) The conditions under which the test vapors are generated should be as like as possible to the conditions found in practice.
- (2) Corrections should be made for variations from the normal barometric pressure.
- (3) The size and dimensions of the cup.
- (4) The size, shape, depth of immersion and exposed part of the thermometer should be definite and in every case the thermometer should be calibrated.
- (5) The oil should never be exposed for any length of time at temperatures greatly higher or lower than the normal temperature.
- (6) The rate of heating on testing should be constant and at a rate of about 1° C. for lamp oils and 3°-5° C. for high flash-point oils.
- (7) The oil should be uniformly stirred during the test.
- (8) The test flame should be of definite size, should be exposed at a fixed distance above the surface of the oil and exposed for a definite length of time.
- (9) All water should be removed from the oil prior to testing.
- (10) In general testing, so far as possible, the effect of the personality of the operators should be eliminated and the manipulation of the tester made entirely mechanical and automatic.

The most accurate tester and the tester that most nearly reproduces actual working conditions should be adopted for official tests. Considering all of the above factors, it is believed that these two testers, the Abel-Pensky and the Pensky-Martens, as modified by the Bureau of Mines, most nearly meet with the desired conditions.

The Bureau of Mines flash testers have been officially adopted by the National Fire Protection Association, the Independent Petroleum Marketers' Association of the United States and are now being considered for adoption by committees on tests of the National Petroleum Association, the American Chemical Society, the American Society for Testing Materials and the International Petroleum Commission.

BUREAU OF MINES
PITTSBURGH

THE TITRATION OF CALCIUM AND MAGNESIUM IN THE SAME SOLUTION

By PAUL J. FOX¹

Received September 9, 1913

Few determinations are more frequently made in chemical laboratories than those of calcium and magnesium, and the writer was led into the following investigation with a view to lessening the labor required for these determinations: The titration of calcium as oxalate with permanganate is, of course, a well known and standard process, and the titration of magnesium as magnesium ammonium arsenate with sodium thiosulfate in acid solution after the addition of potassium iodide has been described by Meade² and by G. B. Frankforter and Lillian Cohen.³

It has occurred to the writer that it might be possible to combine these processes in one operation by first precipitating the calcium as oxalate, and then in the same solution and without filtering, precipitating the magnesium as magnesium ammonium arsenate, filtering off and washing the combined calcium oxalate and ammonium magnesium arsenate, dissolving in acid, titrating the calcium oxalate with potassium permanganate and then the magnesium ammonium arsenate with sodium thiosulfate after the addition of potassium iodide. As will be shown in the sequel, this combined method is perfectly feasible, the two titrations not interfering with each other.

The titration of calcium as oxalate calls for no remark except to observe that the objection that the calcium sulfate formed prevents complete decomposition of the calcium oxalate is not, in the writer's experience, valid. With moderate skill in manipulation, it is always possible to obtain good results.

In the titration of the arsenate, however, certain irregularities were encountered. For example, following approximately the directions in the paper of Frankforter and Lillian Cohen, when 10 cc. portions of a certain solution of ammonium arsenate were acidified, and made up to 100 cc. so that 100 cc. contained about 15 cc. concentrated sulfuric acid, cooled, 5 grams potassium iodide added, and titrated after standing 5 minutes, 21.21, 21.52, and 20.78 cc. thiosulfate solution were required to decolorize the solution. All the portions were, of course, measured out by the same pipette and measured over the same portion of the burette. The figures given are selected from many and are representative of the magnitude of the variations. They were measured out and titrated at different times, a series titrated at the same time showing less variation. The end point was always certain and definite.

Many experiments were made to find the cause and remedy for the irregularities, but to cite the figures in detail would scarcely be profitable. The advantages of the improvements suggested are more or less self evident. The principal causes of irregularity—assuming of course that the iodide used is free from iodate or other substance capable of setting free iodine

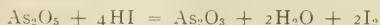
¹ Scientist in Soil Investigations, Bureau of Soils, U. S. Dept. of Agriculture.

² R. K. Meade, *Jour. Am. Chem. Soc.*, **21**, 146 (1899).

³ *Jour. Am. Chem. Soc.*, **29**, 1464 (1907).

in acid solution—are (1) the slowness with which pentavalent arsenic sets free iodine in acid solution; (2) in strong solutions, the escape of iodine before titration; (3) especially the effect of light on setting free iodine from hydriodic acid; and (4) the returning color at the end point.

The setting free of iodine from pentavalent arsenic may be represented by the equation



This reaction proceeds from left to right rather slowly. Fine sand was tried as a catalyzer but with no appreciable accelerating effect. Heating to about 40° accelerated the reaction, but the temperature must be so closely managed to avoid a precipitation of yellow arsenic trisulfide, that it cannot be recommended: too many determinations are lost. Removing the reaction products on the right-hand side of the equation naturally suggested itself. It is not practicable to use sulfuric acid of sufficient strength to take up the water, but it was found distinctly advantageous to add the thiosulfate immediately after the potassium iodide, to a light straw color, and then to allow to stand, for 5 to 6 minutes, before titrating to the end point. This procedure also operates to prevent the escape of iodine before titration.

The principal cause of irregularity, however, was found to be light. Of course, titrations were not made in sunlight, but even the diffused daylight of Washington in summer is sufficient to set free considerable iodine. That the light and not the presence of iodates or other oxidizing bodies sets free the iodine was shown by dissolving five grams of the potassium iodide used in recently boiled acidified water, displacing the air in the flask by carbon dioxide, and allowing to stand for some time in the dark. No color was developed.

The returning color at the end point appears to be caused by the incomplete setting free of the iodine by the arsenic and by light. The reaction $\text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 = 2\text{NaI} + \text{Na}_2\text{S}_4\text{O}_6$ seems to have no tendency, even in the light, to go from right to left.

It was found possible to eliminate the effects of light, or rather to eliminate the irregularities, by placing the Erlenmeyer flask in which the titration was made in the dark during the time it was standing after having had the greater part of the thiosulfate added, and preparatory to completing the titration. Likewise, after bringing to an end point, the flask is allowed to stand in the dark one minute. If there is no return of color the end point has been reached. The darkness was conveniently provided by rolling a hollow cylinder out of black paper and placing it over the flask in which the titration had been made.

In spite of these precautions, however, it is necessary to make a correction for iodine set free otherwise than by arsenate. The correction has the effect of making the variation more nearly uniform. The improvement in results brought about by these precautions is shown by the following experiments: Ten cc. of a solution of ammonium arsenate was diluted to 100 cc. with water containing 15 cc. concentrated sulfuric acid, and 5 grams of potassium iodide added. Sodium thiosulfate (about tenth normal) was added to a light

straw color, and the flask allowed to stand in the dark for about six minutes. The rule was observed to allow eight minutes to elapse between the adding of the potassium iodide and the completing of the titration. Then thiosulfate was slowly added to decolorization, and the flask placed in the black paper cylinder for one minute, and if a color returned, it was discharged. Commonly there was no return of color, if the last drops of thiosulfate had been added slowly. In three experiments, 20.85 cc., 20.82 cc., and 20.80 cc. thiosulfate solution were consumed. In general there was no difficulty in getting check results within one or two drops of tenth normal thiosulfate on titrations of about 20 cc. In this case no correction has been subtracted for light, as the procedure was merely being tested.

The most convenient means of finding the correction for iodine set free by light or by other means than pentavalent arsenic is by titrating with thiosulfate, as described above, two portions of ammonium arsenate solution (of which the exact concentration need not be known) one, say, of 10 cc., and the other of double the amount or 20 cc. If the 10 cc. arsenate required x cc. thiosulfate solution and the 20 cc. required y thiosulfate solution, then the correction is $(2x - y)$ cc. It may be 0.2 to 1.0 cc. Of course the correction may be found by titrating magnesium ammonium arsenate, but it is longer and not necessary. It is not possible to find the correction by making a blank in the ordinary manner, a correction found by such means coming out too low. The following figures show the results of the corrected method of titration of 10 and 20 cc. portions of an ammonium arsenate solution: (The arsenate solution is not the one previously referred to.)

ARSENATE Cc.	THIOSULFATE Cc.	MEAN Cc.
10	20.98	} 20.94
10	20.91	
20	40.83	} 40.92
20	41.02	

From which the correction proves to be $2 \times 20.94 - 40.92 = 0.96$ cc. This correction is unusually large. In general, it will amount to from 0.3 to 0.7 cc.

A solution of calcium chloride free from magnesium and iron was prepared by boiling a solution of calcium chloride with calcium oxide and acidifying the filtrate barely to acid reaction with hydrochloric acid. A solution of magnesium chloride free from iron and calcium was prepared by boiling magnesium chloride solution with magnesium oxide, filtering, evaporating the filtrate with a little ammonium oxalate, taking up with water and a little ammonia, filtering and slightly acidifying the filtrate. Portions of these were taken for analysis. In the case of the calcium chloride solution it was found gravimetrically, each experiment being in triplicate with unusual care, that 25 cc. yielded 0.1283 gram CaO, 50 cc. 0.2575 gram, 100 cc. 0.5158 gram CaO. Thus if we determine the CaO yield directly on 25 cc. CaCl_2 solution, we find that it amounts to 0.1283 gram. But if we take the difference, 50 cc. — 25 cc. = 0.2575 — 0.1283 gram = 0.1292 gram CaO. So also $\frac{1}{3}$ (100 — 25) cc. and $\frac{1}{2}$ (100 — 50) both

equal 0.1207 gram after rounding off the tenth milligrams. Thus 25 cc. of the CaCl_2 solution is equivalent to 0.1207 gram CaO , or 10 cc. = 0.05167 CaO . In all the experiments the conditions of bulk of solution, temperature, and wash water were kept exactly alike, and the 0.0 mg. difference is evidently owing to the solubility of the calcium oxalate under the conditions of the experiment. This source of error is also mentioned by Hillebrand.¹ Strictly speaking, it is an absolute error which should be applied to each determination, but it will not be necessary to apply it if the permanganate is standardized by weighing out pure Iceland spar, especially if the bulk of permanganate used in standardization does not differ very greatly from that consumed in the analysis. In the case of the magnesium chloride solution, no such solubility error was found. By precipitation with ammonium phosphate, each determination being in duplicate:

10 cc. = 0.0391 MgO

20 cc. = 0.0780 MgO

30 cc. = 0.1173 MgO

Average for 10 cc. = 0.03907 MgO

No volumetric method for magnesium, so far as the author knows, can hope to yield so exact results. It must be remembered, however, that in the present case, the magnesium ammonium phosphate was precipitated under ideal conditions, there being present no other salts, and only slightly more than the calculated amount of ammonium phosphate necessary to precipitate the magnesium. Under working conditions this determination is well known to be subject to a serious plus error.² Under working conditions, probably the volumetric method will give as good results as the gravimetric unless special precautions and care are taken with the latter.

For the volumetric solutions the mean of all titrations showed each cc. of permanganate = 0.002816 CaO . For the thiosulfate each cc. = 0.002074 MgO .

METHOD FOR COMBINED DETERMINATION

The combined determination is made in the following manner: Precipitate the iron and alumina with ammonia or basic acetate in the usual manner.³ There must always be sufficient ammonium salts present to prevent a precipitation of magnesia when the solution is made *slightly* alkaline. In the filtrate, precipitate the calcium hot with excess of oxalic acid⁴ and dilute ammonia added slowly, to slight alkaline reaction, a drop of methyl orange having been added to the solution. Then add sufficient ammonium arsenate to precipitate the magnesia, and slowly add ammonia with constant stirring to the *hot* solution until the magnesium am-

monium arsenate comes down, or if so much calcium oxalate is present that this cannot be observed, add about 10 cc. strong ammonia water. Let cool and add 10 to 15 cc. more strong ammonia. Add the ammonium arsenate to the hot solution within a few minutes after the solution has been made slightly alkaline in the precipitation of calcium oxalate, as magnesium oxalate soon begins to come down, which is, of course, one of the sources of error in the standard gravimetric procedure. After the arsenate has been added, it is immaterial how long the determination stands before filtering. Let stand over night,¹ filter and wash thoroughly with dilute ammonia water. The precipitate is then transferred to a 300 to 500 cc. Erlenmeyer flask. If a paper filter has been used, the quantitative transfer is most conveniently made by spreading the paper out on the inner surface of a 4-inch funnel, of which the stem has been bent to rest against the inner wall of the flask into which it has been inserted. The precipitate is rinsed off with hot water, then with dilute acid.² Add 10 cc. sulfuric acid (1 acid to 1 water), make up to about 75 to 80 cc. and titrate hot with permanganate solution. Let cool and add 25 cc. more of the acid. It is well not to have the bulk of the solution much over 125 cc. when about to titrate the magnesia; still, if much lime is present, the 75-80 cc. mentioned above may not be sufficient, in which case, a larger bulk and more acid can be used. These proportions of acid are necessary in order to give a satisfactory end point. Add 5 grams of potassium iodide³ and immediately titrate to a straw color with sodium thiosulfate. Stopper the flask, and cover with black paper, or set in the dark for about 5 minutes. Eight minutes should elapse between the putting in of the iodide and the last part of the titration. Complete the titration drop by drop. Read the end point and place in the dark for one minute. If there is a return of color, discharge it. Usually there will be none if the last drops of thiosulfate have been added slowly. The writer strongly concurs in what Frankforter and Lillian Cohen⁴ say about the use of starch, namely, that it is very much better to do without it. The writer tried four samples of starch, and was unable to obtain any satisfactory end point at all. Methylene blue is also useless as an indicator in the strong acid solution. There is no indefiniteness in the end point when simply the fading out of the brown color of iodine is depended on.

The amount of acid prescribed will be found sufficient when amounts up to 45 to 50 cc. tenth normal thiosulfate solution are required. If more magnesia is present, more acid must be added, which can even be done during the titration if done carefully. It is much better, however, to use a stronger solution of

¹ Bull. 422, U. S. G. S., page 119.

² Hillebrand, *loc. cit.*, p. 128.

³ From a qualitative experiment, it appears to be practicable to precipitate the calcium, add tartaric acid, make alkaline, and precipitate the magnesia with arsenate, the iron and alumina remaining in solution in the well-known combination with alkaline tartrate. Some other hydroxy organic solvents for iron oxide were tried, *e. g.*, sucrose and mannite, but did not work so well. No quantitative experiments were made in this direction. This plan would be convenient where iron and alumina are not wanted, or are determined on separate portions of the material.

⁴ The precipitation of calcium in acid solution yields larger crystals, as many authors have mentioned, and free from material contamination by occluded magnesia.

¹ One determination gave good results after being shaken twenty minutes after cooling, and immediately filtered.

² If too strong acid is used, the filter paper is acted on, giving presumably a cellulose hydrolysis product, which produces a color with iodine. If 50 cc. strong sulfuric acid (sp. gr. 1.84) are mixed with 500 cc. water, and the mixture applied at water bath temperature, all the precipitate will be promptly dissolved and the filter paper not attacked.

³ If much magnesia is present, it is well to add the potassium iodide slowly, as otherwise a precipitate sometimes falls out which does not readily redissolve. Its composition was not studied.

⁴ *Loc. cit.*

thiosulfate, say fifth normal. One cubic centimeter tenth normal thiosulfate solution equals theoretically only 0.002016 magnesia (MgO), so that a fifth normal solution would not be unduly strong. Apply a correction for iodine set free by the light, etc., by titrating as described above 10 cc. and 20 cc. of a solution of ammonium arsenate (of which the exact concentration need not be known—about 20 grams to liter is convenient). If 10 cc. required x cc. thiosulfate and 20 cc. required y cc., then the correction is $(2x - y)$ cc.

It is very important, as the experiments cited show, to standardize the volumetric solutions by weighing out and titrating some suitable compound for the permanganate, pure Iceland spar,¹ and for the arsenate, specially prepared magnesium oxide, or some samples of magnesium ribbon. Very considerable errors will be made by assuming the theoretical values for the solutions.

The following results were obtained:

	CaO taken Grams	Permgt. Cc.	CaO found Grams	MgO taken Grams	Thio- sulfate Cc.	MgO found Grams	Error in Mg.
1.....	0.0517	18.70	0.0527	0.0391	18.32	0.0380	-1.1
2.....	0.0517	18.40	0.0518	0.0781	37.31	0.0774	-0.7
3.....	0.0517	18.38	0.0518	0.1172	56.63	0.1174	+0.2
4.....	0.1292	45.97	0.1295	0.0391	18.49	0.0383	-0.8
5.....	0.1292	45.94	0.1294	0.0781	37.38	0.0775	-0.6
6.....	0.1292	45.86	0.1291	0.1172	56.17	0.1165	-0.7
7.....	0.1292	45.90	0.1292	0.0977	47.36	0.0982	+0.5
8.....	0.1292	45.92	0.1293	0.0977	46.48	0.0964	-1.3
9.....	0.1292	45.64	0.1285	0.0977	46.42	0.0962	-1.5
10.....	0.1292	45.72	0.1287	0.0977	48.00	0.0995	+1.8
11.....	0.1292	45.67	0.1286	0.0977	47.93	0.0994	+1.7
12.....	0.0517	18.42	0.0519	0.1953	95.36	0.1977	+2.4
	1.2404	440.52	1.2405	1.1526	555.85	1.1525	-6.7
							+6.6

The results of the titration of calcium call for no special remark. With regard to the magnesium, it may be stated at once that the writer was unable to obtain the very exact results reported by Meade. Meade, however, worked under ideal conditions as to the composition of his solutions, while the results here set forth were obtained under the conditions existing in actual analysis. The writer's results are, however, comparable with those of Frankforter and Lillian Cohen. In cases of this kind we do better to consider the absolute rather than the relative error. The results of the latter are reported in parts per million of Mg, having been obtained from water analyses in which 500 cc. water were used. Thus the results must have been multiplied by two. In the writer's results, as previously mentioned, the standard for the volumetric solutions is taken from the mean of all titrations, while the volumetric results of Frankforter and Lillian Cohen are in the mean 3.3 per cent higher than their gravimetric results. If we make the results of Frankforter and Lillian Cohen comparable with those of the writer by dividing by two, converting Mg into MgO and adding 3.3 per cent to each gravimetric result, we find that the average error amounts to 1.7 mg. MgO in 84.1 mg. MgO, and that the maximum error amounts to 6.5 mg. MgO in 131 mg. MgO. In the writer's results the average error amounts to 1.1 mg. MgO in 96.0 mg. MgO, and the maximum error to 2.4 mg. MgO in 195.3 mg. MgO. It will

be noticed that the writer's results would be improved by standardizing at two different concentrations. The irregularities seem to be due to a lack of absolute uniformity in the composition of the magnesium ammonium arsenate.

There seems to be no limit in reason to the amount of magnesium which may be titrated, if the concentration of the acid is kept sufficient, but the strength of the thiosulfate solution should be so adjusted—and the principle is, of course, valid in all volumetric work—that not more than 30 to 50 cc. are used in a titration. If it is not so adjusted, the addition of the considerable volume of thiosulfate solution used in the titration so reduces the acid concentration that a good end point cannot be obtained.

The permanganate was standardized with Sörensen's sodium oxalate as supplied by the Bureau of Standards and was found to be 0.0996 normal, which would amount to 0.002794 CaO per cc. For the 440.52 cc. of permanganate used in all the titrations, we should have 1.2309 grams CaO, instead of 1.2404, which would correspond to a loss by solubility of 0.79 mg. per determination. The conditions of each experiment were kept uniform. The thiosulfate solution was standardized by twice sublimed iodine and by permanganate, both according to the directions in Treadwell and Hall.¹ It was found to be 0.1011 normal, corresponding to 0.002038 MgO per cc. or a total of 1.1328 grams MgO instead of 1.1526. This would correspond to an average loss of 1.65 mg. MgO per determination. Whether this loss is caused by solubility or by the magnesium ammonium arsenate as precipitated not corresponding to its formula on the average, the writer does not know. These figures are given to emphasize the necessity of standardizing the volumetric solutions with the same substances and under the same conditions as are used in practice.

This method of determining calcium and magnesium is obviously not adapted to use in making complete rock analysis, nor is any volumetric method.²

Outside of technical uses, there are many cases in soil and rock work where only partial analyses are desired. For example, in a very interesting article by E. S. Bastin,³ it is shown how chemical composition serves as a criterion for identifying metamorphosed sediments. Substantially the only elements considered are iron and alumina, and the ratios MgO/CaO and K₂O/Na₂O. It is believed that the present method would be useful in this sort of work, especially where it is desired to make a large number of determinations. It is also to be noted that sodium and potassium may be determined in the filtrate from the precipitation of calcium and magnesium, the arsenic being volatilized by means of hydrobromic acid as shown by Browning and Drushel.⁴

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

¹ Page 602ff, Vol. II. The standardization by permanganate agrees well with that by iodine, and is much more convenient, even if the permanganate itself has to be standardized with sodium oxalate.

² Hillebrand, *loc. cit.*, p. 121.

³ *Journal of Geology*, **17**, 445 (1909).

⁴ *Am. J. Sci.*, **23**, 293 (1907).

¹ Hillebrand, *loc. cit.*

COMPARISON OF THE KJELDAHL-GUNNING-ARNOLD METHOD WITH THE OFFICIAL KJELDAHL AND OFFICIAL GUNNING METHODS OF DETERMINING NITROGEN

By T. C. TRESCOT¹

Received September 3, 1913

It has been brought to the attention of the Nitrogen Laboratory of the Bureau of Chemistry that the modified method for determining nitrogen, known as the Kjeldahl-Gunning-Arnold method,² can be carried out in a shorter time than the Gunning method or the Kjeldahl method and with as accurate results as either of them. This method is identical with the official Kjeldahl method³ except that 10 grams of

plete oxidation. The reagents have been checked by blanks by all methods. Column 2 gives the number of determinations which were made on a typical sample of each of the substances indicated in column 1.

It will be noted that the results by the Kjeldahl-Gunning-Arnold method carried out with a one and one-half-hour period of digestion are higher than those by the Gunning method for three or four hours, excepting in the cases of cheese and flour, in which they are practically the same. Compared with the results of the Kjeldahl method with three or four hours digestion they are practically the same, excepting in the cases of leather, leather waste, linseed meal, and

DETERMINATION OF NITROGEN BY GUNNING, KJELDAHL, AND KJELDAHL-GUNNING-ARNOLD METHODS

SUBSTANCE	Gunning method				Kjeldahl method				Kjeldahl-Gunning-Arnold method							
	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.
		4 hours.				4 hours.				1½ hours.				4 hours.		
Hair waste.....	10	9.09	8.93	9.01	6	9.09	8.98	9.04	9	9.09	8.98	9.03	10	9.09	8.87	8.98
Dried blood.....	10	8.93	8.70	8.80	10	8.93	8.81	8.88	10	8.98	8.81	8.90	10	8.93	8.81	8.89
Bone meal.....	9	3.26	3.14	3.17	10	3.26	3.14	3.20	9	3.26	3.14	3.19	8	3.26	3.14	3.21
Leather.....	9	6.18	6.01	6.07	10	6.23	6.06	6.12	9	6.26	6.12	6.18	9	6.23	6.06	6.16
Leather waste.....	10	7.69	7.64	7.67	8	7.80	7.69	7.74	9	7.80	7.75	7.79	9	7.80	7.75	7.77
Cottonseed meal.....	9	6.79	6.68	6.74	9	6.96	6.79	6.88	9	6.96	6.85	6.88	10	6.96	6.85	6.91
Linseed meal.....	10	4.97	4.86	4.94	8	5.08	5.00	5.03	10	5.14	5.01	5.08	10	5.14	5.02	5.07
Gelatin.....	8	15.90	15.78	15.87	8	16.11	15.72	15.98	8	16.17	16.06	16.08	8	16.17	16.06	16.10
		2½ hours.				2 hours.				1½ hours.				3 hours.		
Cyanamide.....	9	13.64	13.47	13.56	7	13.59	13.53	13.57	3	13.59	13.59	13.59	7	13.64	13.59	13.61
Beef extract(a).....	3	9.14	9.10	...	3	9.22	9.11	...	3	9.27	9.18	...	3	9.27	9.18	...
Desiccated meat(b).....	3	12.74	12.74	12.74	2	12.86	12.86	12.86	3	12.91	12.86	12.89	3	12.91	12.86	12.89
		3 hours.				3 hours.				1½ hours.				1½ hours.		
Flour.....	8	1.80	1.74	1.76	9	1.80	1.74	1.76	9	1.77	1.74	1.76	9	1.80	1.74	1.77
Bread.....	2	1.99	1.96	1.98					2	2.08	2.05	2.07				
Gluten bread.....	2	10.44	10.36	10.40					2	10.58	10.58	10.58				
Macaroni.....	2	2.25	2.25	2.25					2	2.27	2.25	2.26				
Ground rye hay.....	2	2.47	2.47	2.47					2	2.58	2.53	2.55				
Shorts.....	2	2.50	2.47	2.49					2	2.53	2.50	2.52				
Bran.....	3	2.78	2.75	2.77					3	2.81	2.75	2.79				
	2	2.84	2.84	2.84					2	2.92	2.89	2.91				
Molasses feed.....	2	1.88	1.85	1.87					2	1.94	1.94	1.94				
	3	1.71	1.60	1.66					3	1.77	1.74	1.75				
Milk.....	2	0.528	0.528	0.528					2	0.550	0.547	0.549				
Condensed milk.....	2	1.30	1.30	1.30					3	1.33	1.29	1.31				
	3	1.19	1.17	1.18					3	1.25	1.22	1.23				
	3	1.19	1.17	1.18					3	1.24	1.19	1.22				
Evaporated milk.....	3	1.10	1.08	1.09					3	1.10	1.09	1.10				
	3	1.18	1.17	1.18					3	1.17	1.14	1.15				
	3	1.06	1.05	1.06					2	1.08	1.07	1.08				
	3	1.07	1.07	1.07					3	1.08	1.08	1.08				
		4 hours.														
Cheese.....	3	3.90	3.87	3.89					3	3.93	3.83	3.87				
	3	4.57	4.52	4.54					3	4.60	4.56	4.58				
	3	3.50	3.47	3.49					3	3.49	3.47	3.48				

(a) The maximum and minimum of 3 analyses for 4½ hours by the Kjeldahl-Gunning-Arnold method were 9.27 and 9.18, respectively.

(b) Two analyses for 4½ hours by the Kjeldahl-Gunning-Arnold method gave 12.91 and 12.86, average 12.89.

crystallized potassium sulfate are added as in the Gunning method, and potassium permanganate is omitted. Investigations were carried out on a variety of substances in order to compare more fully this modification with the standard Gunning and Kjeldahl methods.

The following table gives the maximum, minimum, and average percentages of nitrogen found in various substances by means of the different methods, employing the periods of digestion which the experience of this laboratory indicates are necessary to secure com-

plete oxidation. The reagents have been checked by blanks by all methods. Column 2 gives the number of determinations which were made on a typical sample of each of the substances indicated in column 1. It will be noted that the results by the Kjeldahl-Gunning-Arnold method carried out with a one and one-half-hour period of digestion are higher than those by the Gunning method for three or four hours, excepting in the cases of cheese and flour, in which they are practically the same. Compared with the results of the Kjeldahl method with three or four hours digestion they are practically the same, excepting in the cases of leather, leather waste, linseed meal, and

gelatin, in which they are slightly higher. In the case of cyanamide the one and one-half-hour digestion by the Kjeldahl-Gunning-Arnold method gave results (not given in the table) which indicated incomplete oxidation and it was found necessary to heat this substance for two and one-half hours. With this longer period of oxidation the results of the modified method were the same as those of the Kjeldahl and Gunning methods.

The general conclusion from these results is that the Kjeldahl-Gunning-Arnold method with one and one-half hours' oxidation, except in the case of cyanamide, which requires two and one-half hours, gives more concordant and reliable estimations of nitrogen

¹ Chief, Nitrogen Laboratory, Bureau of Chemistry.

² U. S. Dept. Agr., Bureau of Chemistry, *Circ.* 108, p. 15 (1912).

³ U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 107, Rev., p. 5.

than do the official Gunning or official Kjeidahl methods, both of which require from three to four hours for oxidation, depending upon the material.

BUREAU OF CHEMISTRY
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

ORTHO-TOLIDINE AS A REAGENT FOR THE COLORIMETRIC ESTIMATION OF SMALL QUANTITIES OF FREE CHLORINE

By J. W. ELLMS AND S. J. HAUSER

Received August 25, 1913

With the increasing use of very small quantities of chlorine, either free or in the form of hypochlorites for the disinfection of water for drinking purposes, a colorimetric method for the detection and estimation of small amounts of free chlorine is desirable.

STARCH-IODIDE METHOD

The volumetric method in which iodine is liberated from potassium iodide by the chlorine, and the iodine titrated with sodium thiosulfate, using starch as an indicator, offers some difficulties when very small quantities of chlorine are to be determined. Both the sodium thiosulfate and the potassium iodide solutions deteriorate on standing. Frequent standardization of the sodium thiosulfate is always necessary if accurate estimations are to be made. Free iodine is liberated from solutions of potassium iodide on standing, and errors from this source must be constantly guarded against in estimating small quantities of free chlorine. Starch as an indicator in this method is open to an objection on the score of not being sensitive, unless freshly prepared solutions are used. The indefiniteness of the color end point, due to the liberation of free iodine from the potassium iodide, and the consequent deepening of the color are defects which make the detection of small amounts of free chlorine uncertain. Under the most favorable conditions the starch-iodide method is capable of detecting quantities of free chlorine not lower than 0.03 part per million. This method, therefore, for the foregoing reasons lacks reliability for use in determining the residual free chlorine which may be left in the treated water.

ACETIC ACID SOLUTION OF ORTHO-TOLIDINE

The ortho-tolidine test for free chlorine, as suggested by Earl B. Phelps, in which an acetic acid solution of this reagent is used, furnishes a delicate qualitative test, but is open to certain objections for quantitative purposes on account of variations in color produced by waters of different composition.¹ According to this method a one-tenth per cent solution of *o*-tolidine in 10 per cent acetic acid is employed. With two drops of this reagent in 50 cc. of the water containing about 0.05 part per million of free chlorine a yellow color is supposed to be developed. Dittoe and Van Buskirk found that instead of a yellow color developing with very small quantities of chlorine, a green color was produced which changed from green to yellow and finally to deep red as the concentration of the free chlorine was increased. In one instance

when testing for chlorine in a sample of the water supplied to the city of Columbus, Ohio, a light blue color developed on adding *o*-tolidine. No explanation for these color changes is attempted by the above writers. It is apparent, however, that *o*-tolidine could not be very well employed in a colorimetric estimation, unless these color changes were eliminated.

A limited amount of study of the various factors affecting these color changes has been undertaken by the authors, and a reliable mode of procedure for a colorimetric determination worked out. A possible explanation of the reactions involved is offered, which seems to account for some of the color changes, although the authors have not had the opportunity of making a sufficiently thorough investigation to enable them to explain completely all of these complex reactions.

In using the acetic acid solution of *o*-tolidine with small amounts of chlorine, it was found that different shades of color were produced, ranging from a yellowish green to a blue. Although in this test the dyes are produced in an acid solution, nevertheless the variations in the colors formed appeared to be intimately associated with the original degree of alkalinity of the water. Waters that are naturally alkaline from the carbonates of calcium and magnesium, which they contain, or those rendered artificially so by any of the fixed alkalies, act similarly. The higher the original alkalinity of the water containing free chlorine, the bluer is the shade of color produced. The more nearly neutral is the water being examined, the yellower is the tint. In natural waters of moderate hardness, which have not been materially modified by some method of purification, the usual tint obtained is a yellowish green.

By increasing the concentration of the acetic acid a more yellowish green color is produced; but only by adding very large quantities of acid is a yellow color formed. On the other hand the addition of a very small quantity of a highly dissociated acid, such as hydrochloric or sulfuric, produces a deep yellow color with small amounts of free chlorine. This yellow color is not affected by the original degree of alkalinity of the water being tested, nor is the tint modified by any change in the concentration of the acid.

By increasing the amount of free chlorine, the acetic acid solution of *o*-tolidine produces first a solution with a yellowish green color, changing to an orange and then to a deep red. Still larger quantities of chlorine produce a dark red precipitate. Small quantities of bromine and iodine produce, with an acetic acid solution of *o*-tolidine, green-colored solutions. With larger amounts bromine acts as does chlorine, but iodine tends to form a precipitate more readily, and it is of a bluish color.

With increasing concentrations of solutions of potassium bichromate or potassium permanganate, but with no halogens present the acetic acid solution of *o*-tolidine produces first green-colored solutions, then yellow solutions and finally deposits brown-colored precipitates. These precipitates are soluble in hydrochloric acid and give yellow-colored solutions. On the addition of nitric acid to an acetic acid solution

¹ "Report on the Public Water Supply of Cleveland with reference to the Treatment with Calcium Hypochlorite," by W. H. Dittoe and L. H. Van Buskirk, Ohio State Board of Health, *Bull.* 3, No. 1 (January, 1913).

of *o*-tolidine a yellow-colored solution is formed.

The acetic acid solution of *o*-tolidine darkens on standing, and especially so when exposed to the light. Old solutions give slightly different shades of color with small amounts of free chlorine, than do those which are freshly prepared. The green colors produced with small amounts of free chlorine fade within a few minutes, and are probably not reliable for longer than five minutes for colorimetric estimation against standards prepared with known amounts of chlorine. This reagent is sufficiently delicate to detect quantities of free chlorine as low as 0.01 part per million. The objections to making use of the acetic acid solution of *o*-tolidine for the quantitative determination of small amounts of free chlorine may be summed up as follows:

1st. Waters of varying degrees of alkalinity produce different shades of color with similar amounts of free chlorine.

2nd. Fading of the colors occurs within a few minutes.

3rd. Deterioration of the reagent with age, especially in the light.

HYDROCHLORIC ACID SOLUTION OF ORTHO-TOLIDINE

Since the addition of small amounts of highly dissociated acids, such as hydrochloric and sulfuric, was found to give a yellow color with small amounts of free chlorine, when using the *o*-tolidine reagent, and since this color was neither affected by the degree of alkalinity of the water being tested, nor by changes in the concentration of the acid, it led to the preparation of a hydrochloric acid solution of *o*-tolidine in place of the acetic acid solution. The strength of this hydrochloric acid solution was one-tenth per cent *o*-tolidine in a 10 per cent solution of hydrochloric acid. This reagent does not deteriorate on standing. It produces with small quantities of free chlorine a yellow color.

The yellow color is produced uniformly with small amounts of free chlorine, regardless of the soluble constituents of the water being tested. The alkalinity of the water in no way affects the shade or tint produced. The presence of sulfates, chlorides and nitrates of the alkalis and alkaline earth bases do not interfere with the test. The yellow color develops in about three minutes and is permanent for at least one-half hour. There is a good gradation of color for increasing amounts of free chlorine. The test is delicate enough to detect 0.005 part per million of free chlorine.

With large amounts of free chlorine, the hydrochloric acid solution of *o*-tolidine changes from yellow to orange then to red and finally throws down a dark red precipitate. Bromine and iodine both produce yellow-colored solutions with this reagent. Large quantities of bromine behave as does chlorine, but iodine solutions do not appear to form precipitates. Solutions of potassium permanganate and potassium bichromate produce a yellow color with this reagent, which deepens with increased concentration of the above compounds, but do not form precipitates. Nitric acid gives a yellow-colored solution with this reagent, which could be due either to the oxidizing action of the nitric acid, or of the chlorine formed by the oxidation of the hydrochloric acid of the *o*-tolidine solution.

METHOD OF ANALYSIS

The method of making the colorimetric test consists in adding 1 cc. of the one-tenth per cent *o*-tolidine solution in 10 per cent hydrochloric acid to 100 cc. of the water to be tested for free chlorine. When the free chlorine exceeds 3 parts per million it is necessary to use more of the reagent. The water and the reagent are well mixed and are allowed to stand for five minutes. They are then compared with standards of known strength prepared at the same time or with permanent standards as described below. From a solution of chlorine, standardized by means of a *N*/100 thiosulfate solution, a series of standards are prepared by dilution with redistilled water. The strength of the chlorine solution should be determined at the time the standards are to be prepared. The latter must be freshly made and immediately compared with the samples being tested. Water for dilution of standards should be as free from organic matter as redistillation with alkaline potassium permanganate will make it. Ordinary distilled water contains enough organic matter to quickly reduce the chlorine and thus cause it to disappear.

To avoid the difficulties inherent in preparing standards as above described, permanent standards may be made from solutions of copper sulfate and potassium bichromate in sulfuric acid solution. For standards between 0.01 part per million and 10 parts per million the proportionate volumes of the two solutions are given below.

Parts per million	Copper sulfate Potassium bichromate	
	Cc.	Cc.
0.01	...	0.8
0.02	...	2.1
0.03	...	3.2
0.04	...	4.3
0.05	0.4	5.5
0.06	0.8	6.6
0.07	1.2	7.5
0.08	1.5	8.7
0.09	1.7	9.0
0.10	1.8	10.0

NOTE—Potassium bichromate solution: 0.025 gram + 0.1 cc. concentrated sulfuric acid diluted to 100 cc. with distilled water.

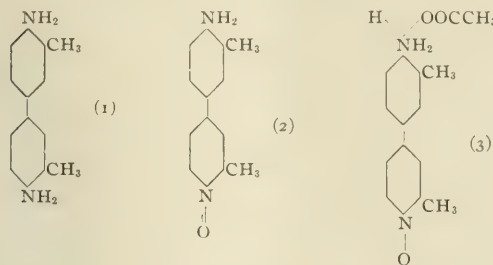
Copper sulfate solution: 1.5 grams $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ + 1 cc. concentrated sulfuric acid diluted to 100 cc. with distilled water.

Standards higher than 0.10 part per million require a stronger potassium bichromate solution; *i. e.*, 0.25 gram + 1 cc. concentrated sulfuric acid diluted to 100 cc. with distilled water.

Parts per million	Copper sulfate Potassium bichromate	
	solution Cc.	solution Cc.
0.10	1.8	1.0
0.20	1.9	2.0
0.30	1.9	3.0
0.40	2.0	3.8
0.50	2.0	4.5
0.60	2.0	5.1
0.70	2.0	5.8
0.80	2.0	6.3
0.90	2.0	6.7
1.00	2.0	7.2
2.00	2.0	12.0
3.00	2.0	21.0
4.00	2.0	30.0
5.00	2.0	39.0
6.00	2.0	46.0
7.00	2.0	56.0
8.00	2.0	63.0
9.00	2.0	70.0
10.00	2.0	75.0

SUGGESTIONS AS TO THE CAUSES FOR COLOR CHANGES

Ortho-tolidine is an organic compound of the formula $C_{14}H_{16}N_2$.¹ It is a homolog of benzidine and is a powder melting at $120^\circ C$. It may be prepared from *o*-nitro-toluene by reduction with zinc dust and sodium hydroxide. The resulting hydrazo-toluene is converted into the *o*-tolidine by boiling with hydrochloric acid. It may be purified in a manner similar to that of benzidine. Its structural formula may be written as at (1):







It is a *p*-2-diamido-*m*-2-dimethyldiphenyl compound, and probably produces dyes of the same general type as those derived from benzidine. Oxidation of *o*-tolidine probably produces a nitroso compound of formula (2): this compound is probably blue in color. Salts of *o*-tolidine upon oxidation produce a yellow dye, a possible formula for the acetic acid salt being (3).

The green color produced by the action of the chlorine on the acetic acid solution of *o*-tolidine is probably a mixture of the blue compound (2) and the yellow compound (3). In the hydrochloric acid solution of *o*-tolidine, HCl is merely substituted for $HOOCCH_3$. The slight dissociation of acetic acid and the hydrolysis of the acetate perhaps account for the slow formation of the yellow dye in the acetic acid solution, while the large dissociation of hydrochloric acid might be the reason for the rapid development of the yellow color in the hydrochloric acid solution.

The red color and red precipitate produced by large amounts of chlorine may be a substitution product of the nitroso compound resulting from the complete oxidation of all the *o*-tolidine present.

Aniline treated with a solution of bleaching powder produces certain color reactions, but it requires a considerable amount of chlorine for their development. Similarly ortho-toluidine forms colored solutions with chlorine, which are likewise slowly developed, although somewhat more rapidly than in the case of aniline. As has been previously noted benzidine readily produces colored solutions with chlorine, similar to those formed with *o*-tolidine. Its sensitiveness to chlorine is much greater than is that of aniline or *o*-toluidine but somewhat less than that of *o*-tolidine.

The colors produced by a solution of bleaching powder in gradually increasing quantities with neutral and with acid alcoholic solutions of aniline, *o*-toluidine, benzidine and *o*-tolidine are shown in the following table:

	COLOR OF PRECIPITATE IN		
	Neutral alcoholic solution	Alcohol and acetic acid.	Alcohol and HCl
Aniline 	Yellow-green-brown	Brown-purple red	Yellow-purple red
<i>o</i> -Toluidine 	Yellow-orange-brown	Purple-blue-red	Purple-red
Benzidine 	Yellow-orange-red	Green-orange-red	Yellow-orange-red
<i>o</i> -Tolidine 	Yellow-orange-red	Green-orange-red	Yellow-orange-red

A blue color reaction produced by the action of hypochlorites on methyl-aniline and ethyl-aniline has been recently reported by Leech.¹ He suggests that the blue dye, possibly a member of the "indo" series of dyes, results from the oxidation of the methyl or ethyl group. It seems to the authors that in the case of *o*-toluidine and *o*-tolidine that the dyes are produced as a result of the oxidation of the amido group, and not the methyl group, since in aniline and benzidine, having no methyl groups, similar dyes are formed by the action of hypochlorites.

CINCINNATI FILTRATION PLANT
CINCINNATI, OHIO

THE QUANTITATIVE ESTIMATION OF GLIADIN IN FLOUR AND GLUTEN

By GEO. A. OLSON
Received July 26, 1913

Since Einhof² separated alcohol-soluble proteins from wheat, rye and barley, much interesting research work has been done on prolamines. It was not, however, until Osborne and Voorhees³ presented a study on the proteins of the wheat kernel that a clear understanding as to the nature of vegetable proteins was established. Of particular interest was the research on gliadin, the prolamine of wheat. It has been further believed that the proportion of gliadin to glutenin determines the quality of the gluten which in turn

¹ "A Color Reaction of Hypochlorites with Methyl-Aniline and Ethyl-Aniline," by Paul N. Leech, *Jour. Am. Chem. Soc.*, **35**, No. 8 (August, 1913).

² See "The Proteins of the Wheat Kernel and Vegetable Proteins," by Thomas B. Osborne. Also *Trans. of the Canadian Institute*, **7**, 1903, by George G. Nasmyth.

³ *Amer. Chem. J.*, **15**, 392 (1893).

determines the quality of a flour for bread making purposes.¹

Following Millon's² work on the quantity of gluten contained in different kinds of wheat, another series of investigations bearing on the relationship of the gluten to the baking qualities of flour was commenced. Heinrichs³ failed to establish any relationship between the gluten and baking quality, but Fleurent⁴ was led to believe that the alcohol-soluble portion of the gluten, rather than gluten, determines the baking qualities of flour. The method adopted by Fleurent for the extraction of gliadin cannot be said to be satisfactory since the diluted alcohol contains potassium hydroxide and potassium hydroxide like sodium hydroxide is a solvent for glutenin as well as for gliadin.

Based upon Osborne's and Voorhees' work, Teller⁵ worked out a method which he used for the estimation of gliadin in wheat at different periods of growth. He, and subsequently Chamberlain⁶ and others,⁷ observed that a part of the alcohol-soluble nitrogen was extracted by salt solution. The writer in his studies on the nitrogen components of wheat flour has confirmed this work. The fact that the quantitative methods which we follow for the estimation of proteins in wheat flour are far from satisfactory, led the writer to carry out a series of experiments, some of the results of which are recorded below.

The strength of alcohol most suitable for the extraction of gliadin from flour, or gluten, has never been determined. It is known that above certain strengths of alcohol little or no gliadin can be extracted, while below this limit all the gliadin can be extracted, provided enough solvent is used. Teller¹ studied the solubility of proteids in different strengths of alcohol and found that while the quantity of nitrogen extracted increased with the dilution of alcohol until a maximum amount of alcohol-soluble nitrogen products had been extracted, solutions containing from 40 per cent to 60 per cent alcohol gave identical results. From 65 per cent to 95 per cent by volume, the per cent of nitrogen products decreased rapidly. Osborne and Voorhees in their work used an alcohol of 0.90 sp. gr. Later Shutt⁸ and Hummel⁹ observed between the range of 60 per cent to 75 per cent alcohol, by weight, that the nitrogen content of flour soluble in alcohol decreased with the increased strength of alcohol. Between 60 per cent and 86.4 per cent alcohol, by weight, Shutt observed the same order of solubility: with 86.4 per cent alcohol only 0.12 per cent nitrogen; compared with 60 per cent alcohol 0.94 per cent nitrogen was noted. Hoagland,¹⁰ working with two samples of flour, observed that more nitrogen was extracted with water than with alcohol of strengths ranging from 10 to 20 per cent by weight. Increasing the strength to

75 per cent by weight, Hoagland found that alcohol of 40 to 45 per cent by weight extracted as much or more nitrogen products than strengths ranging between 60 to 75 per cent by weight. He believes a 50 per cent alcohol by weight to be the logical strength to use. It should be remembered that Osborne and Voorhees separated the gliadin or its nitrogen from the alcohol-soluble nitrogen. The fact that larger quantities of nitrogen-carrying bodies are extracted with weaker alcohols does not prove that larger quantities of gliadin are extracted, yet nitrogen determinations are made and it is assumed that such is the case.

The observations of Kjeldahl,¹ Mathewson,² and Osborne and Harris³ showed the specific rotation of gliadin, $[\alpha]_D - 92$ to be uniformly constant. Snyder⁴ introduced a method for the estimation of gliadin which proved unsatisfactory in the hands of others. Thatcher⁵ was unable to use the method on soft wheat flours. Shaw and Gaumitz⁶ state in their paper that "the gliadin nitrogen should be corrected for the amide nitrogen present, but for most practical purposes this may be neglected," especially "with old and unsound flours a correction must be made for the soluble amide bodies." Chamberlain also is of the opinion that amide compounds soluble in alcohol are considered as gliadin in the proposed methods.

Greaves,⁷ in his thesis work, with the aid of the polariscope, found that 70 per cent alcohol extracted more nitrogen in smaller quantities of flour than where the same quantity of alcohol acted upon larger quantities of flour. Chamberlain recommended that at least 100 cc. of alcohol per 2 grams of flour should be used. In working with alcohol ranging from 60 per cent to 80 per cent by weight, Greaves obtained the largest amount of nitrogen, with a few exceptions, with 70 per cent alcohol. The highest specific rotation $[\alpha] - 89.80$ was observed with 74 per cent alcohol, and he is of the opinion that this is more nearly true gliadin than gliadin extractions made with other strengths of alcohol.

In studies with hot alcohol compared with cold, Chamberlain⁸ obtained more gliadin nitrogen in cold alcohol than in case of hot alcohol. Leach⁹ recommends 100 cc. of 75 per cent hot alcohol per gram of material. Hoagland found that at a temperature of 75° C., and below the latter temperature, there is practically no temperature effect on the amount of nitrogen extracted. Greaves, employing tightly stoppered pressure flasks, obtained higher results with hot alcohol compared with cold.

In the earlier investigations on gliadin the experimental work was directed towards the preparation of pure gliadin, so that it was possible to properly identify and classify it. In the latter researches, when quantitative methods were desired, the sum total nitrogen

¹ *Agr. Gazette N. S. Wales*, Sept., 1896. *Jour. Amer. Chem. Soc.*, **1900**, 263. *Ibid.*, **1905**, 1068. *Compt. rend.*, **1896**, 123, 155.

² *Jour. f. prakt. Chem.*, Bd. **61**, 344 (1854).

³ *Berichte d. Landw. Versuchs. Rostock*, **1894**.

⁴ *Compt. rend.*, **1896**, 327.

⁵ *Ark. Bull.* No. **53**.

⁶ U. S. Dept. of Agr., Bur. of Chem., *Bull.* No. **81**.

⁷ *Ibid.*, *Bull.* No. **90**.

⁸ Central Exp. Farm, Ottawa, Can., **1907**.

⁹ U. S. Dept. of Agr., Bur. of Chem., *Bull.* No. **105**.

¹⁰ *This Journal*, **3**, No. 11, 838.

¹ *Centralbl. Agr. Chem.*, **25**, 197 (1896).

² *Jour. Amer. Chem. Soc.*, **28**, 1482 (1906).

³ *Ibid.*, **24**, 844 (1903).

⁴ *Ibid.*, **26**, 263 (1904).

⁵ *Ibid.*, **29**, 910 (1907).

⁶ *Calif. Bull.*, No. **212**.

⁷ *J. Biol. Chem.*, **9**, 3-4, 271.

⁸ *Jour. Amer. Chem. Soc.*, **28**, No. 11.

⁹ *Food Inspection and Analyses*, p. 232.

extracted by alcohol has been considered pure gliadin. In literature, there is nothing to show that all of the nitrogen compounds present in the alcohol-soluble is the nitrogen of pure gliadin. There is, on the other hand, some indication that a part at least of the nitrogen products is a part of less complex substances than gliadin, *e. g.*, amides. There is some evidence that substances closely allied to gliadin are present and which O'Brien¹ believes "closely merge into one another."

The general methods adopted for the separation of gliadin from its solvent have been either to dilute the alcohol and add salt solution or increase the strength of alcohol by adding absolute alcohol. Osborne states that distilling off the alcohol *in vacuo* causes the settling out of gliadin. This latter method has been made use of by the writer when handling large quantities of material.

But where the quantity of material is small and the exact purity of the material is of secondary importance, the writer has evaporated off the alcohol in the open, thereby causing precipitation or settling out of protein. Owing to the peculiar properties of gliadin and the similar properties of the coagulum it is reasonable to believe that they are one and the same substance. The gliadin, however, is purer than the precipitate due to the fact that it is redissolved and precipitated a number of times. The nitrogen bodies dissolved by the alcohol and not precipitated are non-gliadin bodies which from a quantitative point of view are generally included as gliadin nitrogen.

This means of separating the alcohol-soluble nitrogen materials into two groups offers a satisfactory working basis for the estimation of gliadin in flour or gluten. In some respects such a method is similar to the one in vogue for the estimation of casein in milk.

In order to learn whether or no it was possible to make use of the above method for the estimation of gliadin it was necessary to include with it the estimations for the salt-soluble protein substances found in flour.

In the preliminary experiments a series of four flours were selected. These were first extracted with one per cent salt solution (NaCl), followed by treating the insoluble residue with sufficient 95 per cent alcohol to make an alcohol 70 per cent by volume. A direct 70 per cent alcohol separation was also made. Besides this, 50 cc. aliquot of the direct alcohol-soluble separation was evaporated to within 5 cc., 50 cc. of water added, boiled, and then cooled to room temperature. A heavy coagulum or settling out resulted upon the evaporation of the alcohol and increased in amount upon cooling after the boiling.

An aliquot of the 1 per cent salt-soluble was evaporated to dryness and then extracted with 70 per cent alcohol, in order to remove the gliadin which, according to Teller and confirmed by Chamberlain, is appreciably soluble in 1 per cent salt solution. The residue remaining after the alcohol extraction should be composed largely, if not all, of edestin and leucosin. The alcohol extraction in the dried salt solution should

carry with it the coagulable and non-coagulable nitrogen which was removed by the salt solution.

Nitrogen determinations were made by the straight Kjeldahl method in the flour, the direct extraction of the flour with 70 per cent alcohol, the coagulum in this alcohol-soluble, the alcohol-soluble resulting after the extraction of the flour with 1 per cent salt solution, the salt-soluble extraction and the salt-soluble insoluble in 70 per cent alcohol. The results obtained for the above determinations are recorded in Table I.

TABLE I.—ALCOHOL-SOLUBLE PROTEINS BY DIRECT, INDIRECT AND COAGULATION METHODS

No.	Per cent total nitrogen	Per cent alcohol-soluble nitrogen direct	Per cent alcohol-soluble nitrogen coagulated	Per cent salt-soluble nitrogen	Per cent alcohol-soluble nitrogen in salt-soluble	Per cent alcohol-soluble in nitrogen in the insoluble salt residue	Per cent total alcohol-soluble nitrogen indirect
1	1.47	0.82	0.61	0.40	0.25	0.35	0.60
2	2.07	1.11	0.73	0.45	0.29	0.52	0.81
3	2.18	1.22	0.87	0.47	0.32	0.61	0.93
4	2.73	1.64	1.12	0.61	0.33	0.84	1.17

The data given in Table I give results by the direct process of extracting flour for nitrogen-carrying bodies as well as the reverse process. The results obtained are not comparable with each other in the two methods. More than this, the data show that salt extracts a part of the alcohol-soluble nitrogen-carrying bodies and 70 per cent alcohol by volume applied directly to a flour removes larger amounts of protein than can be accounted for by the indirect method. The excess amount of alcohol-soluble by the direct method possibly has been altered upon evaporating the salt-soluble and hence is no longer soluble in this strength of alcohol. The data further show that a large part of the alcohol-soluble nitrogen-carrying bodies are coagulated when the alcohol is removed and boiled with water. These results further indicate that a part of the alcohol-soluble nitrogen-carrying bodies is estimated as leucosin and edestin when 1 per cent salt solution is used. Similar results were obtained by Chamberlain who extracted the flour with alcohol followed by extracting the alcohol residue with a 5 per cent solution of potassium sulfate. The amount of nitrogen-carrying bodies extracted from the alcohol residue as obtained by him was only one-fifth as much as that obtained by the direct extraction of the flour with 5 per cent potassium sulfate.

Perhaps the most interesting results obtained were the remarkably close agreement between the nitrogen in the alcohol-soluble coagulum and that of the alcohol-soluble nitrogen where the flour had first been extracted with 1 per cent salt solution together with that extracted in the direct salt-soluble. These data add further evidence that alcohol extracts other nitrogenous substances from flour than gliadin and that "gliadin is appreciably soluble in 1 per cent salt solution." In this series of experiments approximately 72 per cent of the total alcohol-soluble nitrogen is gliadin nitrogen

¹ *Annals of Bot.*, 1895, p. 182.

based on either the coagulum nitrogen or the alcohol-soluble nitrogen by the indirect method.

Owing to the close agreement in the nitrogen content in the coagulum compared with the nitrogen content in the alcohol-soluble by the indirect method it appears reasonable to the writer that either one of the two methods mentioned here would be satisfactory for the estimation of gliadin nitrogen. The method for the determination of the coagulable nitrogen is the shortest and the better one to follow of the two and as a result the writer has devoted his time to a study of this method.

As has been stated, the strength of alcohol best suited for gliadin estimation has never been fixed. Greaves believes that a 74 per cent alcohol is the proper strength to use in polariscopic estimations, while variable strengths have been suggested in gravimetric estimations. For this reason it is necessary to determine a strength that would be suitable for the work involved.

Two samples of flours were digested with cold 45, 50, 55, 60, 65, 70, 75, 80, and 85 per cent alcohol by volume and the nitrogen determined in an aliquot of the alcohol-soluble as well as in the coagulum resulting from another aliquot of the alcohol-soluble. Nitrogen determinations were also made in the phosphotungstic precipitates resulting from the coagulum filtrates. The results for nitrogen in the alcohol-soluble, the coagulum filtrate and the sum of the last two determinations are recorded in Table II of this paper.

TABLE II—AMOUNT OF COAGULABLE NITROGEN OBTAINED IN DIFFERENT STRENGTHS OF ALCOHOL

No.	Material	Per cent N in 45 per cent	Per cent N in 50 per cent	Per cent N in 55 per cent	Per cent N in 60 per cent	Per cent N in 65 per cent	Per cent N in 70 per cent	Per cent N in 75 per cent	Per cent N in 80 per cent	Per cent N in 85 per cent
A.	Direct.....	1.23	1.29	1.30	1.30	1.25	1.21	0.99	0.78	0.33
	Coagulum.....	0.87	0.82	0.84	0.84	0.77	0.75	0.61	0.59	0.15
	Precipitated filtrate.....	0.39	0.45	0.42	0.42	0.41	0.39	0.32	0.23	0.14
	Total.....	1.26	1.27	1.26	1.26	1.18	1.14	0.93	0.82	0.29
B.	Direct.....	1.36	1.63	1.63	1.62	1.57	1.45	1.05	0.86	0.16
	Coagulum.....	1.14	1.18	1.21	1.21	1.17	1.08	0.72	0.50	0.02
	Precipitated filtrate.....	0.24	0.37	0.34	0.35	0.35	0.31	0.36	0.26	0.13
	Total.....	1.38	1.55	1.55	1.56	1.52	1.39	1.08	0.78	0.15

There are several things of interest to be noted in the data given in Table II. The per cent of nitrogen obtained in the coagulum after removing the alcohol runs quite uniformly regardless of strengths of alcohol ranging between 50 per cent to 65 per cent inclusive alcohol by volume. From 70 per cent there is a marked decrease in the per cent of nitrogen until at 85 per cent only about 25 per cent of the total nitrogen in the alcohol-soluble is obtained. The per cent of nitrogen in the phosphotungstic acid precipitated filtrate bears a similar relation. The sum of the per cents of nitrogen in the coagulum and phosphotungstic acid precipitate agree fairly well with the per cents of nitrogen obtained by the direct alcohol extraction.

In regard to the per cents of nitrogen-solubles in different per cents of alcohol it will be noted that the

results agree with those observed, first by Teller, and later by other investigators. From these results it appears that a 50 per cent alcohol by volume is satisfactory to use for the estimation of the per cent of nitrogen in the coagulum. The slight variations noted in the totals compared with the results by the direct method are undoubtedly due to analytical error.

The following method was finally adopted for the study of coagulum fraction of the alcohol-soluble. Four grams of flour were digested with 200 cc. of 50 per cent alcohol by volume, shaking the entire contents at intervals of five minutes apart during the first two hours, then allowing to stand twenty-four hours followed by filtering clear. Aliquots of 50 cc. each were taken from the thoroughly mixed filtrate, evaporated slowly to within 5 cc. volume, 50 cc. of water added to each and further evaporated at a temperature near to boiling until contents of beakers approximately amounted to 10 cc., repeating 50 cc. of water were added and again evaporated down to within 35 cc. The beakers were then removed, 25 cc. water added, allowed to cool to room temperature (21°) and finally filtered. In case of turbid filtrates, the filtrates were repeatedly filtered until clear. The coagulum is difficult to remove in most instances, owing to the sticky nature of this substance, and in such cases the mass was gathered by the use of steel spatula and policeman and transferred to filter paper, occasionally using cold, distilled water to facilitate the transferring and washing of the coagulum. Nitrogen determinations were made according to the Kjeldahl method. The proper corrections for paper and reagents were taken into consideration in all determinations for nitrogen.

The filtrates resulting from the separation of the coagulum were treated with sufficient phosphotungstic acid and nitrogen determined in precipitate and filter paper.

In a series of experiments comprising sixty different flours obtained from different sources, representing different climatic zones in the United States, some of which known as spring or winter wheat patents, others straight, or bakers, some of better baking qualities than others, were subjected to the above mentioned method for the determination of gliadin. The average maximum and minimum results for

TABLE III—PER CENT NITROGEN IN ALCOHOL FRACTIONS

	Per cent total nitrogen in flour	Per cent total alcohol-soluble nitrogen	Per cent coagulable nitrogen	Per cent phosphotungstic acid nitrogen	Per cent error	Per cent coagulable	
						Of total N	Alcohol-soluble nitrogen
Average (60)....	1.97	1.105	0.755	0.295	0.033	38.32	68.32
Maximum.....	2.72	1.560	1.210	0.440	0.19	50.0	86.40
Minimum.....	1.31	0.610	0.440	0.120	0.09	31.0	50.50

per cents of total nitrogen in flour, alcohol-soluble nitrogen, coagulable nitrogen in alcohol-soluble and nitrogen in phosphotungstic acid precipitate are recorded in Table III. In addition the per cent of coagulable nitrogen expressed in per cent of total nitrogen in the flour and alcohol-soluble are included.

According to the results summarized in Table III, it will be noted that the per cent of coagulable nitrogen of total nitrogen in the flour is 38.52, while the per cent of coagulable of total alcohol-soluble is 68.32. It is further noted that all of the alcohol-soluble nitrogen is not coagulable nitrogen and that which is not coagulable is precipitated by phosphotungstic acid. If the coagulable nitrogen contains all of the gliadin nitrogen of flour, it will be noted that this nitrogen does not bear any relation to the total alcohol-soluble, nor total nitrogen of the flour.

In connection with this work it was thought desirable to carry out a few comparative tests as to the purity of the coagulum from a nitrogen point of view with the mass obtained in the alcohol-soluble. Four flours from as many different states were selected for this work. The per cent of total solids, per cent of nitrogen in the solids, the per cent coagulum, per cent of nitrogen in coagulum, per cent ash in coagulum, and per cent of sugar in filtrate resulting from the separation of the coagulum are recorded in Table IV.

TABLE IV—PURITY OF ALCOHOL-SOLUBLE COMPARED WITH PURITY OF COAGULUM

	Per cent total solids	Per cent nitrogen in solids	Per cent coagulum	Per cent nitrogen in coagulum	Per cent ash in coagulum	Per cent sugar in filtrate
Kansas.....	10.11	8.61	4.31	13.69	0.11	0.121
So. Dakota.....	12.02	9.90	5.98	14.88	0.12	0.058
Washington.....	11.10	8.47	6.12	12.09	0.23	0.266
New York.....	10.50	5.14	5.18	10.42	0.39	0.244

The degree of purity of the alcohol-soluble based upon the nitrogen content and total solids is approximately less than one-half the purity of pure gliadin

of preparing gluten in dry form which when moistened with water takes on all of the characteristics of the gluten from which it was prepared. It occurred to the writer that it might be well to try the above method for the estimation of gliadin on prepared glutens obtained from flours in which the method had been tried directly. Accordingly, one-half gram lots of 10XX bolted gluten from six different flours were digested with two hundred centimeters of 50 per cent alcohol by volume and the method as described above was followed from this point. The per cent of nitrogen in dried gluten, the per cent nitrogen in the alcohol-soluble, the per cent nitrogen in coagulable of the alcohol-soluble, the per cent nitrogen in the phosphotungstic acid precipitated filtrate, the error in the determinations, and the amount of gluten in 100 grams of flour from which data the grams of nitrogen in the gluten, the alcohol-soluble and coagulable, have been calculated and are recorded in Table V. The per cent of coagulable nitrogen as found in the alcohol-soluble extract of the flour is introduced in the last column for comparison.

When the possible variations in the results for the determinations of dry gluten, the solubility of gliadin in the process of washing the gluten out of the flour, as well as the possible error involved in making nitrogen determinations, are considered it will be noted (Table V) that the per cent coagulable nitrogen found in alcohol-soluble of the gluten compares remarkably closely with the coagulable nitrogen obtained by the direct extraction of the flour with alcohol. In two instances, *viz.*, B. L. and M. 15, the error is somewhat large, but on closer study it will be further noted that the results obtained in the gluten run lower in all instances

TABLE V—PER CENT COAGULABLE NITROGEN IN GLUTEN AND CALCULATED IN PER CENT OF FLOUR

No.	Per cent N in gluten	Per cent N alcohol-soluble	Per cent N in coagulable	Per cent N in phosphotungstic precipitate	Error	Per cent gluten in flour	Per cent gluten N in per cent of flour	Per cent alcohol-soluble in per cent of flour	Per cent coagulable N in coagulable of flour	Per cent found in flour
O. C.....	13.66	6.64	6.32	0.46	+0.12	14.20	1.95	0.94	0.90	0.96
R. W. B.....	13.96	8.56	5.76	2.68	+0.12	9.56	1.33	0.82	0.55	0.56
B. L.....	14.38	6.64	4.96	1.60	-0.08	9.35	1.34	0.56	0.46	0.58
P.....	12.96	6.88	4.88	2.04	+0.04	17.20	2.23	1.18	0.84	0.92
L. C.....	14.24	7.52	6.56	0.96	0.00	11.60	1.65	0.87	0.76	0.69
M. 15.....	14.28	6.48	4.96	1.50	-0.02	12.70	1.81	0.82	0.63	0.74

(17.6 per cent N) and for the coagulum the nitrogen content (av. 12.77) agrees with the nitrogen content of gluten (12.77 per cent N).¹ The per cent of sugar found and the per cent of ash are small and seemingly do not influence the purity of the proteins to any great extent. Just how much fat the coagulum carries was not determined, but from determinations made in non-ether extracted preparations of gliadin sometimes as high as 13.5 per cent of ether extract was found and presumably the larger amount of fat in the coagulating method includes fat in the coagulum which fat, if included in gliadin, would reduce the nitrogen per cent in gliadin to figures practically as low as those obtained by the writer for the coagulum.

In research bearing on the properties of gluten and its effect upon the baking qualities of flour, we have been exceedingly fortunate in working out a method

except one than was the case in the determination in the flour. A possible explanation for the lower results other than those mentioned above may be either that the total alcohol-soluble material contained in the gluten was not entirely extracted or the alcohol-soluble obtained in flour contained other proteins which coagulate with the coagulum and do not combine with the glutenin to form gluten.

At any rate, gluten prepared in the manner described is excellently suited for the preparations of the component proteins of gluten in pure form. The ether-soluble materials can be removed first, then the alcohol-soluble, etc.

It is a recognized fact that gliadin is slightly soluble in water, somewhat in 1 per cent salt solution and practically insoluble in 10 per cent salt solution. Accordingly, one would expect to find a part of the gliadin in solution in the filtrates resulting from the

¹ THIS JOURNAL, 4, No. 3 (1912).

separation of the coagulum of the alcohol-soluble. In the writer's experience it has been found that the coagulum is difficultly soluble in cold water. Further, upon evaporating the filtrates very small quantities of coagulum result which when transformed into the coagulable state remain practically insoluble. The amount of coagulable material which passes into the filtrates must be exceedingly small and in no case has the writer obtained sufficiently large quantities to warrant a determination to be made. From a quantitative point of view, it is safe to assume that practically all of the gliadin nitrogen has settled out or coagulated and the nitrogen bodies present in the filtrates are of less complex form.

Owing to the difficulties met with in transferring the sticky coagulum formed in the method described above and since the nitrogen contained in the coagulum, together with that found in the filtrate, equal the nitrogen found in the alcohol solution, the writer has deemed it a better method of procedure to estimate the nitrogen in the filtrate resulting from the separation of the coagulum and deduct this result from the nitrogen found in the alcohol-soluble extraction to get the gliadin nitrogen contained in the flour. The method for the estimation of gliadin nitrogen would then read as follows:

Digest four grams of flour with 200 cc. of 50 per cent alcohol by volume. Shake the contents at five-minute intervals for the first two hours, then let stand over night and finally filter clear. Determine the per cent of nitrogen in 25 cc. aliquots of the alcohol-soluble. Evaporate slowly 50 cc. aliquots of the alcohol-soluble to within 5 cc. volume, add 50 cc. distilled water, bring near to boil, and continue process until volume has been approximately reduced to 10 cc. Repeating, add 50 cc. of water and boil down to within 35 cc. volume. Allow contents of beakers to cool to room temperature, then filter. If necessary, repeat filter until filtrate becomes practically clear. Estimate the per cent of nitrogen contained in the filtrate and deduct this result from the per cent of alcohol-soluble nitrogen to get the per cent of gliadin nitrogen in the flour.

CONCLUSIONS

I. Alcohol solutions extract two groups of nitrogen-carrying bodies in wheat flour and gluten. Upon evaporating off the alcohol followed by the addition of water, one of the groups, *viz.*, gliadin, separates out, the other remaining in solution.

II. Salt solution of 1 per cent strength extracts a part of the gliadin contained in wheat flour.

III. The gliadin nitrogen obtained by the indirect method is much lower than that obtained by the direct method, but agrees remarkably closely with the results obtained for nitrogen in the coagulum in the alcohol-soluble.

IV. Of the two methods for the estimation of gliadin, the coagulation method is the shorter and is more suitable to use for this reason than the indirect method.

V. Alcohols ranging between 50 per cent to 65 per cent, inclusive, by volume, extract equivalent amounts of coagulum nitrogen. Above 65 per cent

alcohol by volume there is a rapid falling off in the amount of coagulum nitrogen obtainable. Alcohol of 50 per cent by volume has been adopted by the writer for the determination of gliadin nitrogen.

VI. About 68 per cent of the total alcohol-soluble nitrogen is coagulable.

VII. Alcohol-soluble, incoagulable nitrogen is precipitated by phosphotungstic acid. This, together with the coagulable nitrogen, equals the total alcohol-soluble nitrogen.

VIII. In the same flours as much coagulable nitrogen is obtained in specially prepared gluten as in case of the flour.

IX. The easiest and shortest method for the estimation of the gliadin in flour is to estimate the nitrogen in the uncoagulable portion of the alcohol-soluble and deduct this result from the total alcohol-soluble nitrogen.

WASHINGTON EXPERIMENT STATION
PULLMAN

QUALITY OF THE MASSACHUSETTS MILK SUPPLY AS SHOWN BY THE INSPECTION OF THE STATE BOARD OF HEALTH

By HERMAN C. LYTHER

Received August 14, 1913

During the past year an investigation of the milk supply was undertaken with special reference to certain enzyme and other reactions which could possibly differentiate raw milk from pasteurized milk and new milk from old milk. The nature of these reactions and the source of the substances causing them are not yet clearly settled, but a study of the literature shows the following reactions which may be of an enzyme nature:

Raw milk contains a diastase capable of hydrolyzing 0.01 to 0.02 per cent of starch, a catalase which will liberate oxygen from hydrogen dioxide, a peroxidase which will cause hydrogen dioxide to react with certain organic substances, thereby producing colors, and reductases capable of decolorizing methylene blue solutions. Pasteurization has more or less influence upon the above reactions depending upon the temperature of pasteurization and the length of time subjected to this temperature, and the reactions are also modified by the age of the milk.

The reductases are produced by bacteria according to Konning,¹ Seligman,² and Grimmer.³ On the contrary Seligman² states that some reductase may possibly exist in milk as an enzyme. Romer and Sames⁴ question the enzyme nature of reductase and state that it is produced by the destruction of the cells of the mammary glands during milking, as the first milkings have but slight reducing properties and the last milkings are highly reducing.

Sames⁵ is opposed to the enzyme nature of reductase and thinks that the Seligman assumption that the reduction is due to bacteria is too far reaching. Salus⁶

¹ *Milchwirtsch. Zentr.*, **4**, 156.

² *Z. Hyg.*, **58**, 1.

³ *Milchwirtsch. Zentr.*, **6**, 243.

⁴ *Z. Nahr. Genussm.*, **20**, 1.

⁵ *Milchwirtsch. Zentr.*, **6**, 462.

⁶ *Arch. Hyg.*, **75**, 371.

is of the opinion that reductase is a product of cell transformation. Openheimer¹ states that reductase has nothing to do with bacteria and is difficult to distinguish from bacterial reductases.

The peroxidase according to Jensen² comes from the animal and is not formed by growing bacteria in milk. This is confirmed by Konning,³ Kooper,⁴ and Fred.⁵ Bordas and Touplain⁶ claim that this reaction is due to the casein or to calcium caseinate. They heated milk to 80°, 100°, and 120°, and after centrifuging obtained a cream giving a positive reaction, a skimmed milk giving a negative reaction and a precipitate giving a positive reaction when macerated with water, the heated milk before centrifuging giving a negative reaction. Sarthou⁷ and Meyer⁸ were unable to obtain these results, the latter stating that the results of Bordas and Touplain were not reliable and the reaction obtained was due to foreign dirt. Nicolas⁹ disagrees with Bordas and Touplain but thinks that the casein plays an important part in the reaction. Hesse and Kooper¹⁰ state that the peroxidase reaction is due to alkalinity; when milk is heated its alkalinity is decreased and it will give no reaction with the reagents. The heating according to Kooper¹¹ causes a precipitation of the calcium salts. Grimmer¹² is of the opinion that the peroxidase reaction is due neither to inorganic catalyzers nor to alkaline reaction but is a function of the milk albumin or is due to a substance allied to it which appears to be a protein or is absorbed by the albumin.

Milk catalase according to Fred¹³ and Kooper¹⁴ is of bacterial origin. Kooper states that catalase

tase test is carried out in two ways: with a methylene blue and formaldehyde solution and with a methylene blue solution without formaldehyde known as F. M. reductase and M. reductase, respectively. The formaldehyde causes an acceleration in the time of reduction, fresh milk reducing the F. M. solution in a few minutes and the M. solution in several hours. According to Barthel¹ fresh milk containing 10,000 bacteria per cc. decolorized the M. solution in 11 hours, and the same milk four days old containing 47,500,000 bacteria per cc. decolorized in 14 minutes. He also states² that when the reduction takes place in less than one hour the milk has more than 10,000,000 bacteria per cc. and when the reduction requires from 1 to 3 hours the number of bacteria is from 10 to 4 million per cc. Barthel is of the opinion that milk decolorizing methylene blue in less than one hour is bacterially too impure for food and that good commercial milk should require at least three hours for decolorization.

Angelici³ states that there is no absolute parallelism between the methylene blue reduction and number of bacteria, but that this test is well adapted to sanitary control. Fred⁴ states that most but not all milk bacteria reduce methylene blue, and that milk reducing methylene blue in from one hour to 15 minutes contains from 15 to 50 million bacteria per cc. and milk requiring seven hours or more contains less than 1 million bacteria per cc.

Giffhorn⁵ has made a study of these reactions and his results are given in the following table. The peroxidase reaction was performed with active guaiac solution:

TABLE I—ENZYME REACTIONS OF MILK ACCORDING TO GIFFHORN

Character of milk	Guaiac reaction	M. reductase	F. M. reductase	Diastase	Catalase
Fresh and normal	Positive		5-12 minutes	Digests 0.01 to 0.02 per cent starch	5-70 mm.
Too old for use	Positive		1-5 minutes	Normal	High
Too old for use		Less than 1 hour	1-5 minutes	Low	Low
From diseased udders		Less than 1 hour	Slow	Digests 0.024 per cent starch	High
Heated above 72° was high in bacteria before heating and has stood a considerable time	Negative	Less than 1 hour	Less than 1 hour	None	High
Heated from 65°-72°	Positive			None	

passes into the cream, that its growth increases with the acidity up to 40 or 50° of acid and then decreases. This is confirmed by Faitelowitz¹⁵ who states that the decrease is due to the lactic acid formed and if the acid is neutralized, the catalase will still be active.

On account of their probable bacterial origin, the reductase and catalase reactions are of value in investigating the hygienic quality of milk. The reduc-

Another property of milk of hygienic significance is its ability to coagulate with alcohol. If 95 per cent alcohol is added to milk in increasing quantities it will eventually cause coagulation. As coagulation is caused by the development of acid in the milk it is possible by using the correct strength and amount of alcohol to differentiate between milk above and below a certain acidity. The usual procedure is to add to the milk an equal volume of 68 per cent alcohol by volume. Milk which gives a precipitate under these conditions is sour enough to curdle when boiled.

According to Henkel⁶ fresh milk does not coagulate with an equal or a double volume of 68 per cent alcohol or with an equal volume of 70 per cent alcohol. Suzinger⁷ as a result of two years' work states that an equal

¹ Arb. Egl. Inst. experim. Therap. zu Frankfurt a. M., 1908, 75.

² Rev. gen. lait., 6, 85.

³ Milchwirtschl. Zentr., 4, 196.

⁴ Z. Nahr. Genussm., 20, 564.

⁵ Centr. Bakt. Parasitenk., II Abt., 35, 391.

⁶ Compt. rend., 149, 1057. Ann. Fals., 2, 193. 8th Intern. Congr. Appl. Chem., 18, 69.

⁷ Compt. rend. soc. biol., 68, 434.

⁸ Arb. Kais. Gesundh., 34, 115.

⁹ Bull. soc. chim., 9, 266.

¹⁰ Z. Nahr. Genussm., 21, 385.

¹¹ Ibid., 23, 1.

¹² Milchwirtschl. Zentr., 2, 295.

¹³ Centr. Bakt. Parasitenk., II Abt., 35, 391.

¹⁴ Z. Nahr. Genussm., 20, 564.

¹⁵ Ibid., 21, 294.

¹ Z. Nahr. Genussm., 15, 385.

² Ibid., 21, 513.

³ Clin. Vat., 34, 388.

⁴ Centr. Bakt. Parasitenk., II Abt., 35, 491.

⁵ Diss., Bern, 1909.

⁶ Milchwirtschl. Zentr., 3, 387.

⁷ Ibid., 5, 292.

volume of 68-70 per cent alcohol coagulates colostrum, milk from cows far along in lactation, milk from diseased udders as well as milk otherwise abnormal, and possibly milk from cows calving prematurely, but fresh normal milk does not usually coagulate with 68-70 per cent alcohol.

Barthel¹ says the reaction indicates souring with great certainty, and Rammstedt² states that it is a good preliminary test for freshness of market milk. Bolle³ says it is not always trustworthy, as some milk will coagulate with alcohol and will not upon boiling. Fendler and Borkel⁴ prefer to use a double volume of 50 per cent alcohol. Morres⁵ has improved the test by adding alizarin to the alcohol. The alizarin is an indicator and the colors produced vary from lilac-red in fresh milk through the browns to a yellow in sour milk. This overcomes the objection of Bolle, by giving an additional indication of the amount of acid present.

The following table is given by Morres:

TABLE II—RELATION BETWEEN ACIDITY AND ALCOHOL PRECIPITATION IN MILK

Acidity Degrees Soxhlet- Henkel	Color of alizarin	Nature of precipitate with 68 per cent alcohol	Nature of the milk
7.0	Lilac-red	No precipitate	Normal and fresh
8.0	Pink	Very fine precipitate	Beginning to sour
9.0	Brownish red	Fine precipitate	Sourness in- creasing
10.0	Reddish brown	Precipitate	Critical state
11.0	Brown	Heavy precipitate	Coagulates on boiling
12.0	Yellowish brown	Very heavy precipitate	Coagulates on boiling
14.0	Brownish yellow	Very heavy precipitate	Coagulates on boiling
16.0 and above	Yellow	Very heavy precipitate	Coagulates on boiling

In the investigation made in this department the reductase, peroxidase, and alcohol precipitation reactions were employed; the details of the methods are as follows:

Reductase Reaction.—Schardinger's Test⁶ (F. M.): Twenty cc. of milk are mixed in a test tube with 1 cc. of a solution containing 5 cc. of a saturated alcoholic solution of methylene blue and 5 cc. of 40 per cent formaldehyde in 190 cc. of water. The contents of the tube are covered with a layer of liquid petroleum to prevent access of air, and the tube is then placed in a water bath at a temperature of 45° to 50° C. Raw milk will decolorize this reagent in less than 20 minutes; pasteurized milk will take a longer time.

Schardinger Test (M): This is carried out in the same manner as the F. M. reaction except that the reagent consists of 5 cc. alcoholic methylene blue solution and 195 cc. of water.

Peroxidase Reaction.—(a) Rothenfusser's Test:⁷ Dissolve 1 gram of *p*-phenylenediamine hydrochloride in 15 cc. of water. Dissolve 2 grams of crystallized guaiacol in 135 cc. of 96 per cent alcohol. Mix these

solutions and keep in an amber-colored bottle. To 10 cc. of milk add 0.5 cc. of the above reagent and 3 drops of 3 per cent hydrogen dioxide. A blue-violet coloration is developed in raw milk and if the milk has been heated to a sufficiently high temperature no color is produced. (b) *The Benzidine Test:*¹ Dissolve 4 grams of benzidine in 100 cc. of 96 per cent alcohol. To 10 cc. of milk add 1 cc. of this reagent, 3 drops of 30 per cent acetic acid and 2 cc. of 3 per cent hydrogen dioxide; a blue coloration is produced with raw milk and none with milk heated to a sufficiently high temperature.

Alcohol Precipitation Test: Dissolve 0.3 gram of alizarin in one liter of 68 per cent alcohol (by volume). To a measured quantity of milk in a test tube add an equal volume of the reagent and shake.

The following experiments were undertaken to determine the influence of time and temperature of pasteurization upon these tests.² Five one-pint portions of known purity raw milk were gradually heated (rise of temperature about 2° C. per minute) in a water bath to temperatures of 60, 65, 70, 75 and 80° C. The samples were held at these temperatures for thirty minutes and portions removed every ten minutes. Portions were also removed when the temperature reached 40° and 50°. All these portions were subjected to the Schardinger, Rothenfusser and benzidine reactions and upon a few, bacterial counts were made. The results, including the examination of a sample of commercially pasteurized milk which had been heated to a temperature of 63° C. and held there for 35 minutes, are shown in the following tables:

TABLE III—SCHARDINGER TEST (F. M.). THE FIGURES SHOW THE MINUTES REQUIRED TO DECOLORIZE THE SOLUTION

Temp. of milk	Time held				
	0	10 min.	20 min.	30 min.	35 min.
20°	5				
40°	5				
50°	6				
60°	7	8	9	10	
63°					— ^a
65°	9	12½	16	21	
70°	12	20	85	—	
75°	40	—	—	—	
80°	—	—	—	—	

a — = no decolorization in several hours.

TABLE IV—BACTERIA PER CC.
Time held

Temp. of milk	0	10 min.	20 min.	30 min.
20°	18,000			
40°	180			
50°	120			
60°				60
65°				
70°	40			30
75°				
80°	Spores only			Sterile

Three identical samples of milk, pasteurized by being heated to 63° and held there for 35 minutes, were obtained from a milk contractor. The samples were kept in the refrigerator and a new bottle opened

¹ Z. Nahr. Genussm., 21, 513.

² Z. öffent. Chem., 17, 441.

³ Z. landw. Versuch., 13, 292.

⁴ Z. Nahr. Genussm., 21, 477.

⁵ Ibid., 22, 459.

⁶ Ibid., 5, 1113.

⁷ Milchweirtsch. Zentr., 6, 468.

¹ Z. Nahr. Genussm., 16, 172.

² This experimental work was performed with the collaboration of Mr. Lewis I. Nurenberg, Asst. Analyst of the Mass. State Board of Health.

TABLE V—ROTHENFUSSER REACTION

Temp. of milk	Time held			
	0	10 min.	20 min.	30 min.
20°	+			
40°	+ _a			
50°	+			
60°	+	+	+	+
65°	+	+	+	+
70°	+	faint	faint	faint
75°	— _a	—	—	—
80°	—	—	—	—

_a + = color produced. — = no color produced.

TABLE VI—BENZIDINE REACTION

Temp. of milk	Time held			
	0	10 min.	20 min.	30 min.
20°	+ _a			
40°	+			
50°				
60°	+	+	+	+
65°	+	+	+	+
70°	faint	faint	very faint	very faint
75°	— _a	—	—	—
80°	—	—	—	—

_a + = color produced. — = no color produced.

each day and tested. The results are given below:

	F. M.	Benzidine test	Rothenfusser test	68 per cent alcohol
1st day.....	—	faint	+	no ppt.
2nd day.....	—	+	+	no ppt.
3d day.....	10 min.	+	+	no ppt.

From the above experiments we may conclude that

and the alcohol precipitation test, there does not appear to be an exact parallelism. This may be due to the fact that pasteurization increases the time of the M. as well as the F. M. reduction, and subsequent souring may not develop sufficient reductase to reduce methylene blue within one hour. The following table has been prepared from the results of examination of 77 samples of milk, all of which reduced methylene blue and 48 of which gave precipitates with 68 per cent alcohol:

TABLE VII—RELATION BETWEEN ALCOHOL PRECIPITATION AND M. REDUCTASE

Time of reduction of methylene blue	Color of precipitate with 68 per cent alcohol and alizarin
30 minutes and above	No precipitate
25 minutes	Reddish brown precipitate
20 minutes	Brownish red precipitate
15 minutes	Brown precipitate
10 minutes	Brownish yellow precipitate
5 minutes and less	Yellow precipitate

This shows that the alcohol precipitation method is less sensitive in detecting old milk than the M. reductase reaction, but it is easier to perform, and if a precipitate is given, the sample no doubt is or has been high in bacteria.

The following tables give the statistics of the examinations of milk during the year ending February 28, 1913:

TABLE VIII—SUMMARY OF MILK STATISTICS

Month 1912	Number above stand- ard (a)	Number below stand- ard	Total samples collected	Skimmed samples marked	Skimmed samples not marked	Watered sample	Pasteurized samples	Pasteurized samples below standard	Per cent of skimmed samples not marked	Per cent of watered samples	Per cent of pasteurized samples	Per cent of pasteurized samples below stand- ard	Per cent of total sam- ples below standard	Samples giving ppt. with 68 per cent alcohol	Pasteurized samples giving ppt. with 68 per cent alcohol	Samples reducing methylene blue in 30 min. to 1 hour	Samples reducing methylene blue in less than 30 minutes	Per cent total samples giving ppt. with alcohol	Per cent pasteurized samples giving ppt. with alcohol	Per cent samples reducing M. in 30 min. to 1 hour	Per cent samples reducing M. in less than 30 min.
March.....	270	43	313	3	1	3	82	7	0.3	1.0	26.2	8.5	13.7	18	4	5.8	4.9
April.....	281	96	377	..	5	6	61	16	1.3	1.6	16.2	26.2	25.5	34	3	9.0	4.9
May.....	304	109	413	1	5	19	24	5	1.2	4.6	5.8	20.8	26.4	25	1	6.1	4.2
June.....	341	169	510	1	5	29	36	8	1.0	5.7	7.1	22.2	33.2	16	3.1
July.....	275	195	470	2	1	25	7	2	0.2	5.3	1.5	28.6	41.5	23	1	4.4	14.5
August.....	295	154	449	1	17	4	45	3	3.8	0.9	10.0	6.7	34.3	39	5	12	39	8.7	11.1	2.7	8.7
September.....	311	139	450	3	..	13	61	10	..	2.9	13.5	16.4	30.9	28	1	15	39	5.6	1.4	3.3	8.6
October.....	397	127	524	6	7	9	73	8	1.3	1.7	13.9	11.0	24.2	29	7	5	26	5.5	10.4	0.9	5.0
November.....	247	87	334	1	8	17	50	12	2.4	5.1	15.0	24.0	26.1	12	1	1	7	3.6	2.0	0.3	3.6
December.....	365	34	399	2	5	3	85	6	1.5	0.9	21.3	7.1	8.5	2	..	2	0.5	0.5
1913																					
January.....	276	120	396	1	5	42	50	7	1.3	10.6	12.6	14.0	30.6	20	..	1	9	5.3	..	0.3	2.3
February.....	250	70	320	..	8	25	39	5	2.5	7.8	12.2	12.8	21.9	10	2	3	2	3.0	5.1	0.1	0.1
Totals.....	3612	1343	4955	21	67	195	613	89	1.4	3.9	12.4	14.5	27.2	256	25	37	124	5.2	4.1	1.3	4.3

(a) Legal milk standard in Massachusetts: 12.15 per cent solids; 3.35 per cent fat

it is impossible to detect commercially pasteurized milk by means of the peroxidase reaction, but it can be detected within two days by the Schardinger reaction. The impracticability of the benzidine and Rothenfusser tests as applied to market milk is shown by the fact that but 7 out of a total of 2470 samples of Massachusetts market milk gave a reaction for teated milk. Of these same samples, 348 were pasteurized according to the Schardinger test which is more in accord with the conditions of the Massachusetts milk supply.

Although there is a relation between the M. reductase

A study of the summary of Tables VIII and IX shows that of 4955 samples examined, 262 or 5.3 per cent were adulterated, 67 of which were skimmed and 195 contained added water. Ten hundred and eighty-one or 21.6 per cent of the total samples were below the legal standard and could not be declared adulterated. Of the total samples 613 or 12.4 per cent were found to be pasteurized according to the Schardinger F. M. reaction of which 89 or 14.5 per cent were below the legal standard.

The commercial pasteurized milk is as a rule prepared on a large scale and represents mixed milk

TABLE IX—QUALITY OF AVERAGE MILK

Month 1913	Average of all samples				Average of samples not declared skimmed or watered				Average of raw samples not declared skimmed or watered				Average of pasteurized sample not declared skimmed or watered						
	Solids		Fat		Number	Solids		Fat		Number	Solids		Fat		Number	Solids		Fat	
	Per cent	Per cent	Solids not fat Per cent	Per cent		Per cent	Per cent	Solids not fat Per cent	Per cent		Per cent	Per cent	Solids not fat Per cent	Per cent		Per cent	Per cent	Solids not fat Per cent	Per cent
March	12.61	3.76	8.85		366	12.66	3.80	8.86		224	12.68	3.82	8.86		82	12.57	3.72	8.85	
April	12.68	3.86	8.82		366	12.74	3.90	8.84		306	12.82	3.95	8.87		60	12.43	3.74	8.69	
May	12.46	3.86	8.60		388	12.67	3.91	8.73		364	12.68	3.94	8.74		24	12.47	3.78	8.69	
June	12.33	3.73	8.60		475	12.42	3.78	8.64		445	12.42	3.78	8.64		30	12.47	3.73	8.74	
July	12.21	3.72	8.49		442	12.33	3.77	8.56		435	12.33	3.77	8.56		7	12.29	3.66	8.63	
August	12.34	3.76	8.58		427	12.71	3.91	8.80		382	12.68	3.89	8.79		45	12.88	4.09	8.79	
September	12.46	3.77	8.69		434	12.54	3.83	8.71		375	12.58	3.82	8.76		59	12.38	3.81	8.57	
October	12.69	3.84	8.85		502	12.77	3.91	8.86		429	12.76	3.89	8.87		73	12.82	3.95	8.87	
November	12.65	3.87	8.78		308	12.81	3.96	8.85		258	12.83	3.97	8.86		50	12.69	3.84	8.85	
December	12.94	3.94	9.00		389	12.99	3.99	9.00		304	13.05	4.01	9.04		85	12.75	3.90	8.85	
1913																			
January	12.45	3.82	8.63		348	12.75	3.94	8.81		299	12.78	3.97	8.81		49	12.59	3.77	8.82	
February	12.57	3.80	8.77		287	12.76	3.89	8.87		250	12.77	3.91	8.86		37	12.67	3.80	8.87	
Totals and Averages.	12.56	3.82	8.74		4672	12.67	3.88	8.79		4071	12.68	3.88	8.80		601	12.62	3.84	8.78	

rather than milk from individual cows and therefore should always be above the standard unless for some unknown reason an unusual amount of low-grade milk which is produced on many of the farms is run into the mixer. The analyses of the samples of milk from one of the milk corporations shows that with the exception of those few samples which for removal of cream have resulted in prosecution, the per cent of solids and of fat followed the seasonable variation of milk for that year as shown by our average analysis of all the good samples. In many localities, however, small dealers buy milk from these contractors to mix with their own supply which is insufficient to supply their customers and which may be naturally below the standard. Another way to account for below standard pasteurized milk is that many small dealers buy pasteurized milk and add water to it, and others buy pasteurized skimmed milk to mix with a high-grade whole milk, thereby producing below standard milk which would give a reaction for heated milk and in which the adulteration could not be detected if skillfully performed.

The pasteurized samples showed less variation in solids and less adulteration than the total milk. The variation in solids of the total, raw, and pasteurized samples is shown in Table X from which it may be seen that the percentage of samples with total solids between 12.15 and 13 per cent is greatest in pasteurized milk and least in raw milk.

There is a popular opinion prevailing that the large dealers are manipulating their output by adding skimmed milk, this opinion originating, no doubt, from the fact that this form of adulteration could be carried out successfully if judiciously performed. The figures in Table IX would indicate that this opinion is wrong. The average milk free from adulteration had a total solid content of 12.67 per cent and fat content of 3.88 per cent. This was reduced to 12.56 per cent solids and 3.28 per cent fat (the average of the total milk samples) by the addition of 0.39 per cent of water and the removal of 0.41 per cent of the cream (calculated from the composition of the average adulterated sample, 10.5 per cent solids, 2.6 per cent fat repre-

sented the addition of 10 per cent water and the removal of 23 per cent of the fat). The average of the pasteurized milk is 12.62 per cent total solids and 3.84 per cent fat which is lower than the average raw milk by 0.06 in solids and 0.04 in fat. This does not indicate watering but may be accomplished by the addition of 0.5 per cent of skimmed milk. It does not seem feasible that a large corporation would do this to such a slight extent as the resulting profit of about 0.1 per cent would no doubt be offset by the cost of manipulation. That the fat is lower in the average pasteurized milk than in the average raw milk is probably due to the fact that large dealers separate their cream as a rule from milk of an unusually high fat content, thereby leaving for the trade, milk of slightly lower fat content than the average.

TABLE X—VARIATION IN MILK SOLIDS

	Above 15 per cent	Between 14 and 15 per cent	Between 13 and 14 per cent	Between 12.15 and 13 per cent	Between 11 and 12.15 per cent	Between 10 and 11 per cent	Between 9 and 10 per cent	Between 8 and 9 per cent	Below 8 per cent
Total samples:									
Number	66	257	1081	2366	1125	125	47	14	10
Per cent	1.3	5.0	21.2	46.5	22.1	2.5	0.9	0.3	0.2
Raw samples:									
Number	59	235	963	2000	1048	110	42	12	9
Per cent	1.3	5.3	21.5	44.6	23.4	2.5	0.9	0.3	0.2
Pasteurized samples:									
Number	7	22	118	366	77	15	5	2	1
Per cent	1.1	3.6	19.3	59.7	12.5	2.5	0.8	0.3	0.2

The sale of pasteurized milk is increasing, and notwithstanding that some authorities declare pasteurized milk inferior to raw milk in many respects, it seems that pasteurization is the only solution of the problem of furnishing the public in large cities with a wholesome supply of milk. These cities are so remote from the source of production that the milk is often 72 hours old before it is delivered to the consumer. In the localities where pasteurized milk is sold, about 18 per cent of the samples collected were found to be pasteurized and in the area of greater Boston 621 samples were collected in Boston, Brookline, Cambridge, Chelsea, Everett, Malden, Milton, Newton, Revere, and Somerville of which 211 or 34 per cent

were pasteurized. This is, no doubt, below the true figure on account of the fact that the samples are taken uniformly from the different dealers and not in proportion to the size of their routes; the dealers selling the most milk are without doubt those who sell the pasteurized milk, while the man with the small route generally sells raw milk.

The number of adulterated samples are about the same as found in past years. The laboratory records would indicate that there is more watering done by the producer and more skimming is practiced by the small retailer. The adulteration of milk is not as a rule carried on by the same men. We make but few complaints in court alleging a second offense, for after one prosecution the convicted person either ceases the adulteration, or else goes out of the business. The actual market conditions are better in this respect than our figures show because we collect such a large number of samples from suspected persons. No doubt less than 2 per cent of our milk supply is subject to adulteration.

The alcohol precipitation test showed that 5.2 per cent of the total samples and 4.1 per cent of the pasteurized samples were sufficiently old when they reached the laboratory to curdle on boiling. The results of the M. reductase test showed that 5.6 per cent of the samples collected during seven months were too old to use as food when they reached the laboratory. If these samples could have been tested at the time of taking, the figures would have been lower during the summer months but not much difference could have been expected during cold weather. The pasteurized samples were better in this respect than the raw samples. These figures are higher than would be consistent with a thoroughly hygienic milk supply for if 94 per cent of the samples reached the laboratory in good condition the other 6 per cent collected at the same time would have done so if fresh. An example of very old milk was shown in the samples furnished to a contractor, which were nearly sour when they reached the laboratory, about two hours after being delivered by the producer. It is fortunate that these conditions are unusual or it would be impossible for the consumers in congested districts to obtain any sweet milk.

SUMMARY

1. It is possible to detect commercial pasteurized milk by the Schardinger reaction but not by the peroxidase reaction.

2. The amount of pasteurized milk on the market is greatest in the large districts.

3. The average quality of the milk is considerably above the legal standard.

4. The average quality of the pasteurized milk is very slightly below that of the raw milk but this does not appear to be due to adulteration.

5. Pasteurized milk shows less fluctuation in composition than raw milk, and the percentage of samples below standard is less of the former.

6. Fresh milk will not coagulate with an equal volume of 68 per cent alcohol.

7. Ninety-four per cent of the samples delivered

at the laboratory gave reactions for fresh milk; the balance was too old for use as fresh milk.

I wish to acknowledge my indebtedness to my assistant Mr. Lewis I. Nurenberg for collaboration in the experimental and routine work, and to Mr. Henry N. Jones for making the bacterial counts.

LABORATORY OF FOOD AND DRUG INSPECTION
MASS STATE BOARD OF HEALTH
BOSTON

THE DETECTION OF GELATIN IN SOUR CREAM

By ARMIN SEIDENBERG

Received August 4, 1913

The usual method for the detection of gelatin in food products such as milk or cream and that adopted provisionally by the United States Department of Agriculture¹ consists in the removal of the proteids with acid mercuric nitrate and the precipitation of the gelatin in the filtrate with picric acid. It, however, has been frequently noticed that a sweet cream which gave no precipitate with picric acid would, after souring, show quite a perceptible turbidity on its addition, often heavy enough to lead to the assumption that gelatin was present. It seems most probable that this is due to protein decomposition products not precipitated by the acid mercuric nitrate. G. E. Patrick, in an address on "The Detection of Thickeners in Ice Cream,"² made before the 24th Annual Convention of Official Agricultural Chemists, speaks of what is probably the same or a very similar decomposition product, often found in ice cream after it has soured. He is not certain as to the exact nature of this substance, but believes it to be due to the action of bacteria. He finds that this "pseudo-gelatin," as he calls it, forms a precipitate with picric acid similar to that formed by gelatin under the same conditions and mentions that there is no method known for distinguishing the one from the other. His suggestion, that formaldehyde be added in the laboratory to prevent the bacterial action which produces this decomposition product, is of course not applicable to creams received sour.

The picric acid precipitate from the sour cream is flocculent, resembling $\text{Al}(\text{OH})_3$ in form and settles quite rapidly, while that due to gelatin is small and granular, much like BaSO_4 in form, settles very slowly and on shaking the test tube thoroughly will coalesce in large lumps leaving the solution almost clear. While these differences are quite well defined, the large number of sour cream samples received in this laboratory made a method leaving less room for doubt, in the detection of even small amounts of gelatin, very desirable. After some experimenting I found that there was a sharply defined difference between the solubilities of the two precipitates in hot, neutral water. While both precipitates are soluble on heating in slightly acid solutions, only the gelatin picrate is soluble in hot, neutral water alone. The picric acid precipitate from the sour cream is seemingly entirely insoluble in hot water, after all the picric or other acid has been removed.

To 10 cc. of the cream are added an equal volume

¹ U. S. Dept. Agr., Bull. 107 (rev.), p. 121.

² U. S. Dept. Agr., Bull. 116, p. 24.

of acid mercuric nitrate, the mixture shaken, 20 cc. of water added, again shaken and filtered after 5 minutes. To the filtrate an equal volume of picric acid is added when if gelatin or the soluble decomposition products from the sour cream are present, a precipitate is formed. This is the method mentioned in *Bulletin 107* of the U. S. Dept. of Agriculture.

In order, definitely, to determine the nature of this precipitate, proceed as follows: Cork test tube which should be a large one, and shake very thoroughly. In this way the gelatin picrate will coalesce and filtration be much more rapid. If possible allow to stand for some time after shaking; most of the liquid can then be siphoned off. The precipitate after being brought on to the filter is washed with water containing two to three drops of ammonium hydroxide to 100 cc. until the washings are slightly alkaline to litmus, and then with neutral water until the washings are neutral to litmus. This will remove all excess of picric acid. The precipitate is then transferred to a small beaker and 10 to 20 cc. distilled water added and heated to boiling. If the precipitate is very small in amount it need not be taken from the filter paper, but both can be boiled together.

Filter hot into a test tube. The filtrate will contain the gelatin picrate but not the precipitate derived from the proteids in the sour cream. Cool this filtrate and add an equal volume of picric acid, when, if gelatin was present in the original cream, a decided precipitate will be formed. When large amounts of gelatin are present the solution may become turbid on merely cooling.

In order to determine the delicacy of this method, 25 cc. of a 1 per cent solution of gelatin containing 0.25 gram of gelatin were added to 50 grams of sour cream. The sour cream thus contained only 0.5 per cent of gelatin, which had little thickening effect on it. By using 20 to 25 cc. of this cream instead of 10 cc. as above the presence of the gelatin could be determined with certainty. The above method has been in use in this laboratory for some time and has been found to work satisfactorily, provided the conditions described are obtained. Even smaller quantities of gelatin than this can, of course, be detected by using a larger amount of the original sample.

CHEMICAL LABORATORY
DEPARTMENT OF HEALTH
NEW YORK CITY

A STUDY OF THE COMPOSITION OF CIDER VINEGARS MADE BY THE GENERATOR PROCESS

By L. M. TOLMAN AND E. H. GOODNOW

Received August 18, 1913

When an investigation of the composition of cider vinegar was undertaken by the Bureau of Chemistry about four years ago, a study of the literature on the subject showed that the existing data were composed almost exclusively of analyses of vinegars made by the old barrel process. The authenticity of the two or three samples of generator vinegars reported was not beyond question because of the extreme difficulty of obtaining true samples of such vinegar. There was practically no analytical basis on which the purity

of a given cider vinegar could be determined, and only the most obvious adulterations or substitutions could be detected with certainty. Apparently authentic cider vinegars were reported as containing amounts of solids varying from 1.18 to 8.00 per cent of ash from 0.19 to 0.57 per cent with the other constituents in the same general proportions. A review of the extensive data on fermented ciders, however, showed no such wide variations in composition, and plainly indicated that this marked difference in the composition of cider vinegars was due not to a similar difference in the composition of the raw material, but rather to the method of manufacture. As a new and scientifically controlled process of manufacture had become widely established, and was the source of practically all of the "commercial" cider vinegar on the market, it seemed probable that the product prepared by this process might differ perceptibly from the "barrel" vinegars, and this study was projected with this idea in view.

The essential differences between the barrel method and the generator method of making cider vinegar will be apparent from a brief description of these processes. The conversion of apple juice into vinegar in the barrel was, until recent times, the generally accepted method in this country. Although no longer used for the preparation of cider vinegar in large amounts on a commercial scale, it is still very largely employed on the farm as the source of the family supply. The general procedure is as follows: The juice expressed from the apples is allowed to ferment in a barrel, usually of 40 to 50 gallons capacity, until practically all of the sugar has been changed into alcohol, and the resulting hard cider stored in some dark place, frequently a cellar, where the formation of acetic acid takes place gradually. Under the most favorable conditions the conversion into vinegar is slow. The long period of storage required gives opportunity for infection by harmful organisms, with the development of mal-fermentations, which frequently change the character and composition of the product to a marked degree. The conditions of storage, temperature, cleanliness of the barrel and surroundings are factors entering largely into the quality of the finished vinegar. The simplicity of the method as regards mechanical features is more than offset by the disadvantages of an uncontrolled acetification.

The rapid or generator process is carried on in this country in a very uniform practice which may be outlined as follows: Large quantities of apples are pressed and the juice collected in tanks, holding from 200 to 1,000 barrels where it is allowed to ferment until the sugar is almost completely removed. It is obvious that this alcoholic fermentation on a large scale in contrast to the fermentation on a small scale in the barrel, tends to produce a uniform product. The hard cider thus obtained is run over the generators, which consist of upright cylindrical tanks filled with beech shavings, corn-cobs, rattan, or some similar porous material saturated with strong vinegar. The alcohol is converted almost immediately into acetic acid. The entire process is under exact control, and

can be completed in a very short time compared with the old method. There is practically no opportunity for mal-fermentations to develop and their occurrence would be readily detected. Fully 90 per cent of the cider vinegar made on a commercial scale in the United States is manufactured by this generator process.

It was impossible to establish a fair standard for judging the purity of generator vinegars on the basis of the existing analytical data on barrel vinegars. Before such a standard could be established some data with reference to the composition of generator vinegars must be available and the changes taking place during this method of acetification clearly understood.

from the generators, thus practically establishing a chemical control of the manufacture. The amounts of cider and vinegar used for the feed were carefully measured so that its composition could be accurately calculated. By carrying this experiment over a period of about two months and running some 40,000 gallons of cider over the generators, some interesting and conclusive figures were obtained.

At the beginning of this experimental run the shavings in the generators were saturated with vinegar made from the cider used in the previous run just completed. Before vinegar representative of the new tank of cider could be obtained, it was, therefore, neces-

TABLE I—ANALYSES OF CIDERS AND VINEGARS FROM TANKS 1 AND 2

CIDER AND VINEGAR		Date	1912	Alcohol by volume Per cent	Solids, Grams per 100 cc.	Total Fehling reducing bodies, Grams per 100 cc.	Total sugars as invert Grams per 100 cc.	Non-sugars, Grams per 100 cc.	Ash, Grams per 100 cc.	Alkalinity of soluble ash, Cc. N 10 acid per 100 grams	Total acids as acetic Grams per 100 cc.	Fixed acids as malic Grams per 100 cc.	Ash in non-sugars Per cent	Pentosans, Grams per 100 cc.	Glycerol Grams per 100 cc.	
Tank 1:																
CIDER:																
First day's run	Jan. 18	7.9	3.05	0.57	2.48	0.34	39.0	0.48	0.15	13.7	0.153	0.31			
Eighth day's run	Jan. 25	7.8	3.09	0.58	2.51	0.35	39.8	0.50	0.18	13.9	0.156	0.29			
Eleventh day's run	Jan. 29	7.8	3.09	0.58	2.51	0.35	39.2	0.48	0.17	13.9	0.158	0.31			
Fourteenth day's run	Feb. 1	7.8	3.07	0.57	2.50	0.34	38.6	0.46	0.19	13.6	0.165	0.30			
Vinegar from previous run used to start this tank, generated		Jan. 17	0.38		2.45	0.69	0.43	2.02	0.34	35.6	5.75	0.04	16.8	0.176	0.27	
VINEGAR:																
First day's drip	Jan. 18	0.40	2.48	0.58	0.41	2.07	0.34	36.4	5.73	0.04	16.4	0.179	0.28			
Third day's drip	Jan. 20	0.41	2.56	0.59	0.41	2.09	0.34	36.8	5.72	0.05	16.2	0.176	0.27			
Sixth day's drip	Jan. 23	0.45	2.54	0.63	0.45	2.09	0.33	37.6	5.71	0.05	15.8	0.180	0.29			
Eighth day's drip	Jan. 25	0.40	2.59	0.68	0.48	2.11	0.34	36.8	5.91	0.05	16.1	0.181	0.28			
Tenth day's drip	Jan. 27	0.46	2.70	0.70	0.50	2.20	0.33	37.4	5.85	0.06	15.5	0.180	0.27			
Thirteenth day's drip	Jan. 30	0.46	2.76	0.70	0.52	2.24	0.33	36.6	5.76	0.06	14.7	0.195	0.29			
Sixteenth day's drip	Feb. 2	0.42	2.79	0.74	0.55	2.25	0.34	37.2	5.76	0.07	15.1	...	0.28			
Tank 2:																
CIDER:																
First day's run	Feb. 3	7.75	2.78	0.37	2.41	0.35	38.4	0.50	0.19	14.5	0.120	0.30			
Ninth day's run	Feb. 11	7.7	2.76	0.36	2.40	0.35	36.8	0.48	0.20	14.6	0.111	0.31			
Fourteenth day's run	Feb. 16	7.6	2.73	0.35	2.38	0.35	36.6	0.48	0.20	14.4	0.114	0.31			
Seventeenth day's run	Feb. 19	7.6	2.72	0.33	2.39	0.38	39.6	0.52	0.22	13.8	0.118	0.29			
VINEGAR:																
Second day's drip	Feb. 4	0.43	2.81	0.77	0.56	2.25	0.35	37.2	5.74	0.08	15.5	0.183	0.28			
Eighth day's drip	Feb. 10	0.43	2.79	0.73	0.53	2.26	0.36	38.4	5.80	0.07	15.9	0.175	0.28			
Thirteenth day's drip	Feb. 15	0.40	2.80	0.72	0.53	2.27	0.36	38.8	5.98	0.06	15.9	0.178	0.29			
Seventeenth day's drip	Feb. 19	0.37	2.78	0.72	0.52	2.26	0.35	38.4	6.02	0.07	15.5	0.172	0.29			
Vinegar made from following tank		Feb. 27	0.35	2.69	0.69	0.49	2.20	0.33	38.4	6.02	0.07	15.0	0.161	0.27		

Accordingly, arrangements were made with a favorably situated cider vinegar factory where the so-called "single-run" generator system was used. In this system the cider is mixed with a slightly larger quantity of strong vinegar to reduce the alcoholic content of the feed to such an extent that a single passage through the generator would completely convert the alcohol in the mixture into acetic acid. This factory was so arranged that all of the 60 generators in operation were fed from a central supply tank system and all of the finished vinegar was collected in one central receiving tank. Thus by determining the composition of the cider and vinegar which were mixed to supply the generators, and finally of the vinegars produced, the changes taking place during the conversion of cider into vinegar could be closely followed.

In a small laboratory established at the factory, certain determinations, such as solids, ash, sugar, acidity, alcohol and color, were made. Each day samples were taken of the cider, of the vinegar used to mix back for the feed and of the finished vinegar coming

sary that this vinegar should be completely displaced. As 3 or 4 barrels of vinegar were held absorbed in the packing material of each of the generators, several days would be required before such displacement would normally occur. Another factor which would retard the securing of a vinegar characteristic of this tank of cider lay in the method of feeding the generators. The cider stock was not fed "straight," but instead first mixed with a slightly larger volume of vinegar. For the first day's feed, January 18, vinegar from the drip of January 17 was used for this "mixing back," and each day the vinegar for this purpose was taken from the drip of the preceding day. With this system, it can readily be seen that considerable time must elapse before the vinegar dripping from the generators would be characteristic of the cider stock being fed, especially if there was much difference in the composition of the cider stock and of the vinegar from the previous tank.

In the preceding table a sufficient number of analyses of the ciders and vinegars taken at intervals during

the running of Tanks 1 and 2 has been given to show the changes in composition observed. Each tank contained about 20,000 gallons of cider which was practically of constant composition from the first pumpings to the last, so that for the purpose of comparison a slight variation need not be considered.

Although the vinegar produced on the first day of the experimental run, January 18th, did not differ perceptibly from that of the previous day, decided changes were noted as the operations continued. The total acidity showed a good average yield of acid and remained nearly constant for the entire period, varying only 0.3 gram during the run of the two tanks. Less than 0.5 per cent alcohol remained unconverted in the finished vinegar coming from the generators.

The fixed acids are noticeably affected by the acetification process. The cider of Tank 1 contained about 0.15 gram fixed acids and the vinegars mixed back for the feed 0.04 gram, so that the feed had a fixed acid content of about 0.10 gram. The vinegar coming from the generators contained 0.04 gram fixed acids, and, although the amount increased to 0.08 gram as the run progressed, due to a similar proportional increase in the fixed acid content of the cider, there was a loss of approximately 60 per cent in the generators. This elimination of fixed acids during the acetification process is shown graphically by the curves in Fig. 1.

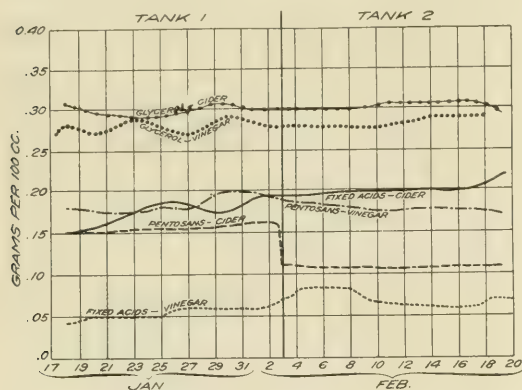


FIG. 1.—VARIATIONS OF FIXED ACIDS, PENTOSANS, AND GLYCEROL DURING CONVERSION OF CIDER INTO VINEGAR

There appears to be a very uniform and constant loss during acetification. In this respect the generator method produces effects similar to the barrel process, in which the fixed acids gradually disappear during the conversion of the cider into vinegar. As the sweet cider probably contained from 0.3 to 0.4 gram of fixed acids, it is apparent that the loss of fixed acids in both the alcoholic and acetic fermentations is very large.

The most notable change was in the content of solids. The first day's drip showed 2.48-grams while the feed had 2.72 grams, calculated from the proportions of carefully measured cider and vinegar used, and the cider itself 3.05 grams. Thus the vinegar coming from the generator contained 0.24 gram less solids than the feed running onto the generator, and 0.57 gram less than the cider stock. This apparent reduction of

solids in the generator during the acetification process is readily accounted for when the mechanical features of the process are taken into consideration. In each of the 60 generators at least 200 gallons of vinegar were held in the shavings, making approximately 12,000 gallons of vinegar in the series of generators at the start. To each generator every day were fed 40 gallons of mix, containing approximately 18 gallons of cider. The vinegar of this mix had practically the same composition as the vinegar in the generators, the vinegar from the previous day's drip being used for making up the feed. Thus each day a 40-gallon

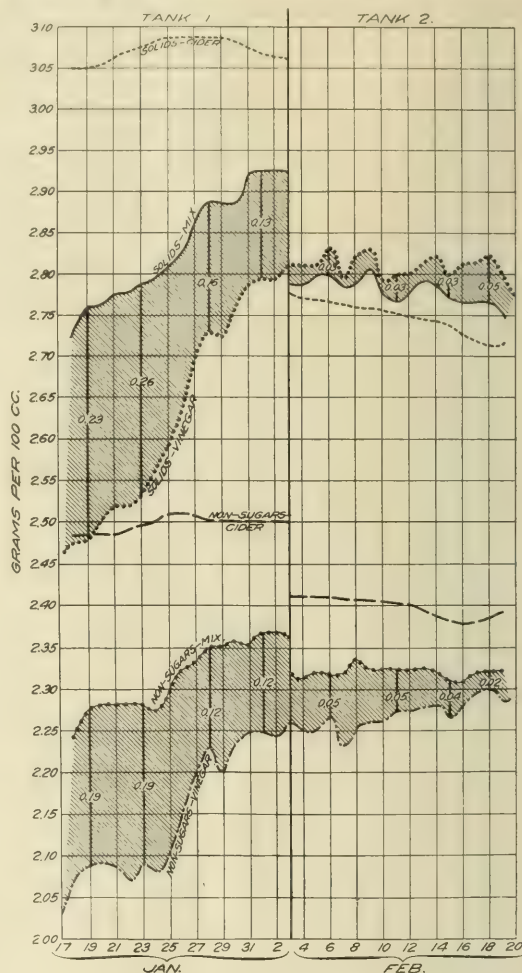


FIG. 2.—CURVES FOR SOLIDS AND NON-SUGARS

feed containing only 18 gallons of the cider was run into at least 200 gallons of vinegar in the generator, and 40 gallons of this mixture dripped out. Consequently only a slight change in the composition of the vinegar dripping from the generator could be expected from day to day, because of the comparatively small volume of the cider fed. When it is borne in mind that there were but 20,000 gallons of cider in Tank 1

and at least 12,000 gallons of vinegar to be displaced in the generators before a vinegar truly characteristic of this cider could be obtained, besides the retarding effect of mixing back each day with a more than equal amount of vinegar from the drip, it is evident that the changes observed must be gradual. That such was the case is shown by the analyses given in Table I and the curves in Fig. 2.

It will be noted that the solids in the vinegar showed an almost uniform daily increase, gradually approaching the solids content of the cider. At the end of 17 days' run on this tank, when the last of the cider had been fed on, the vinegar of the drip contained 2.79 grams solids, an increase of 0.31 gram during the run of this tank, or an average increase of nearly 0.02 gram per day.

The following tank of cider was much lower than the first in solids, having a content of 2.78 grams. The vinegar dripping from the generators contained 2.81 grams solids and the mix for the first day of the run, February 3, 2.78 grams. Thus at the beginning of the run of this tank the solids content of the mix being fed to the generators was practically identical with both that of the vinegar soaked in the shavings, and the cider stock being used, in sharp contrast with the wide differences noted at the start of the run of Tank 1. Were there any appreciable loss of solids in the generator during the acetification process, it would be plainly apparent under these conditions.

From the analyses given in Table I and the curves in Fig. 2, it will be noted that the solids content of the vinegar was almost constant during the run of this tank, and very slightly in excess of the solids in the mix, showing conclusively that there is no appreciable loss of solids in the generation of vinegar by this method. The variations observed in the running of Tank 1 were due mainly to the lag caused by the mixing back with vinegar of a different composition and by the large amount of vinegar of a different composition in the generators when the experiment began. The results indicate that if Tank 1 had been much larger, containing perhaps 40,000 gallons, and the experiment could have been continued for two weeks longer, a vinegar of practically the same composition as the cider would have come from the generator. This is shown clearly by the curves for the solids in Fig. 2. In the case of Tank 1, where the solids of the cider and of the vinegar soaked in the generator, varied widely, there is a decided rise in the curves for both vinegar and mix, these two curves approaching each other. In the case of Tank 2, in which the solids of the cider and the vinegar retained in the generators were practically the same, the curves show no appreciable change during acetification.

The variations in the non-sugar solids during acetification were similar to those already noted in case of the total solids. The cider of Tank 1 had a non-sugar content of 2.48 grams, while the vinegar from the previous day's drip and the vinegar which was absorbed in the filling material of the generator contained only 2.02 grams of non-sugars, and the mixture of cider and vinegar run onto the generators con-

tained 2.22 grams. Thus at the beginning of the experimental run the vinegar coming from the generator and retained in the generator contained about 0.2 gram non-sugars less than the mix fed to the generators and 0.46 gram less than the non-sugar solids in the cider. As the run progressed the non-sugars in the finished vinegar increased gradually, as will be seen from the curves in Fig. 2, approaching the amount present in the feed; but this increase is not quite as rapid as the increase in the total solids.

In the case of Tank 2, the non-sugar content of the cider was 2.41 grams, and that of the vinegar coming from the generator 2.25 grams, so that the mixture of the two going onto the generator contained 2.33 grams. During the run the non-sugar solids in the drip increased very slightly, the vinegar containing 2.26 grams at the end of the run or only about 0.05 gram less than the mix being fed on, but it is probable that this slight loss is more apparent than real. The non-sugars are the resultant of the difference between the total solids and the total sugars, calculated as invert sugar, and any error in the determination of either of these constituents would affect the result for the non-sugars. The total sugars are determined after inversion by their reducing power on Fehling solution. There is present in cider vinegars a substance formed during the acetification which reduces alkaline copper solutions, and thus interferes with the estimation of the sugars by the usual reduction method. Attention was called to the presence of this substance by Mr. Balcom, associate referee on vinegar, in his report to the Association of Official Agricultural Chemists. It was, of course, necessary to modify the method for determining the sugars to eliminate the reducing effect of this substance, which was easily accomplished as it is volatile and readily distilled off by repeated evaporations of the vinegar to a small volume on a steam bath. The following procedure was adopted for the determination of the sugars: 50 cc. of the vinegar were evaporated on the steam bath to 10 cc., and two additions of 10 cc. water with subsequent evaporations to 10 cc. made. This solution was then made up to volume and the reducing sugars determined in the usual manner. From the difference between the Fehling reduction of the vinegar direct and after evaporation, the volatile reducing bodies can be approximated quantitatively in terms of their reducing power. A direct determination can also be made on the distillate from vinegar. For this purpose 100 cc. of the vinegar were distilled down to 10 or 15 cc., 100 cc. of water added and a second distillation made, the two distillates being kept separate. The Fehling reduction was made on the distillates and on the residue made back to volume, following the same procedure as in the determination of invert sugar. The results calculated to grams invert sugar from the Fehling reduction for a few samples of the vinegars from these runs are given in Table II.

It is quite apparent that the presence in vinegars of a substance with a reducing power equivalent to 0.15-0.20 gram invert sugar would cause an appreciable error in the determination of the sugars, and conversely,

TABLE II.—FEBLING REDUCING BODIES
(Calculated as invert sugar)

Vinegar of	Direct after inversion, Grams per 100 cc	After evaporating times Grams per 100 cc	On residue from distil- lation, Grams per 100 cc	Distillate		Total Grams per 100 cc	Total reducing bodies in residue and dis- tillate Grams per 100 cc
				First 100 cc Grams per 100 cc	Second 100 cc Grams per 100 cc		
Jan. 22	0.62	0.45	0.44	0.13	0.01	0.14	0.58
Jan. 23	0.65	0.45	0.46	0.15	0.01	0.16	0.62
Jan. 24	0.66	0.48	0.48	0.14	0.01	0.15	0.63
Jan. 28	0.68	0.50	0.52	0.13	0.02	0.15	0.67
Feb. 6	0.77	0.56	0.55	0.16	0.01	0.17	0.72
Feb. 8	0.77	0.56	0.56	0.16	0.02	0.18	0.74
Feb. 11	0.73	0.53	0.55	0.14	0.01	0.15	0.70
Feb. 13	0.73	0.53	0.53	0.14	0.02	0.17	0.70
Feb. 17	0.73	0.52	0.53	0.16	0.02	0.18	0.71

the non-sugars, by the Fehling reduction method. Our subsequent work on cider vinegars has shown that these bodies are frequently present in still larger amount. Although their exact composition has not been determined, they appear to be of an aldehyde nature, not acetaldehyde as might be inferred from its close relation to ethyl alcohol and acetic acid, but some more complex derivative.

The examination of daily samples of the vinegars made in these experimental runs showed an average of 0.18 gram of these volatile reducing bodies calculated as invert sugar in the finished vinegar, while in the ciders there are none. The formation of these bodies in the generation of vinegar has undoubtedly given rise to the idea that there is an increase in sugars during the process of converting cider into vinegar. In all probability this error in the determination of the sugars is the explanation of the abnormally low non-sugar solids occasionally reported in analyses of vinegars made a number of years ago. After carefully correcting for the amount of volatile reducing bodies present, there actually appears to be a slight increase in the amount of sugar present in the vinegar, as determined by reduction, over that present in the cider.

During the experimental run the total sugars in the vinegar made from Tank 2 decreased from 0.56 to 0.52 gram, while the mixture fed onto the generators contained 0.47 gram, showing a slight increase of sugars which can be accounted for only on the ground of the actual development of reducing bodies. This increase is probably due to the increase in pentosans, which was particularly noticeable in the run of Tank 2, the cider of which contained 0.12 gram of pentosans, while the vinegar coming from the generators contained 0.18 gram, an increase of nearly 50 per cent (see Fig. 2). The small amount of invert sugar present in the fermented cider is not appreciably affected during the acetification, nor are the ash, the ash constituents, or the alcohol precipitable bodies noticeably influenced by the passage through the generator. There is an appreciable loss of color, which, however, largely returns to the vinegar on storage. This loss of color was not observed in the experimental runs with other kinds of generators in other factories; apparently it is associated with the small-sized type of generator used in this plant. The glycerol content of the cider and of the finished vinegar remained practically con-

stant throughout the whole experimental run, as will be seen by noting the curves of Fig. 1. The difference between the glycerol in the cider and in the finished vinegar is very slight, and as this variation is undoubtedly due partly to the factor of the vinegar introduced from the previous run the actual loss in acetification is negligible.

The actual yield of acid was almost constant throughout the run, although considerably below the theoretical yield. Theoretically, 1 part by weight of alcohol or 1.26 parts by volume of alcohol should yield 1.304 parts by weight of acetic acid. As the cider of Tank 1 contained approximately 7.85 per cent by volume of alcohol and 0.23 gram per 100 cc. of acetic acid, the theoretical yield would be calculated as follows:

CALCULATION OF ACID YIELD

Tank 1

	Grams of acetic acid
Theoretical yield:	
7.85 per cent alcohol by volume in cider.....	8.12
Acetic acid in cider.....	0.23
Total.....	8.35
Yield in practice:	
Average of vinegar for run.....	5.75
Actual yield is 68.9 per cent of theoretical yield	

Tank 2

	Grams of acetic acid
Theoretical yield:	
7.60 per cent alcohol by volume in cider.....	7.87
Acetic acid in cider.....	0.31
Total.....	8.18
Yield in practice:	
Average of vinegar for run.....	5.78
Actual yield is 70.6 per cent of theoretical yield	

These calculations and all comparisons between the ciders and vinegars have been made without allowing for any loss in volume by evaporation in passing through the generator. Under normal conditions of working, the loss from this source is not material.

The percentage of ash in the non-sugar solids of the cider in Tank 1 was 13.7 and of the vinegar at the start 16.8. Only fractional variations in this ratio were observed during the run of this tank, and the drip at the end contained 15.1 per cent of ash in the non-sugars. The cider in Tank 2 contained 14.5 per cent

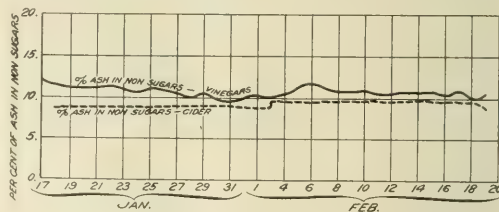


FIG. 3.—PERCENTAGE OF ASH IN NON-SUGARS

of ash in the non-sugars, and the vinegar during the run varied from 15.5 to 15.9 per cent. The slightly higher percentage of ash in the non-sugars of the vinegar was undoubtedly due to the slight apparent loss of non-sugars during acetification already discussed in connection with the increase in pentosans and total Fehling reducing bodies. There appears to be a very constant relation between the amounts of non-sugar

solids and ash which is of decided value in detecting the addition of ash material in the case of adulterated or imitation vinegars. The curves showing the variations in this ratio for these runs have been plotted in Fig. 3.

CONCLUSIONS

The results of this investigation show conclusively that vinegar manufactured by the generator process is uniform in its composition; as uniform as the cider—from which it is prepared—in which respect it differs materially from the vinegars manufactured by the old barrel process. With the exception of the conversion of the alcohol into acetic acid there is but little change in the composition of the cider as it is being converted into vinegar. The most marked difference, other than the oxidation of the alcohol into acid, is the elimination, or, perhaps, destruction of the fixed acids. Here there appears to be an almost constant loss during acetification. On the other hand, there is a considerable formation of pentosans in the generator. No appreciable loss in solids or non-sugars takes place, and the other constituents are practically unaffected. The amount of glycerol in the cider remains almost unchanged by its passage through the generator, and, as it is a product of the alcoholic fermentation, it is an important factor for the detection of adulteration in commercial vinegars. The percentage of ash in the non-sugar solids is remarkably constant, varying only within slight limits, and is of decided value as a standard for judging the purity of cider vinegars.

The results indicate plainly that, given the composition of a hard cider to be used in the manufacture of vinegar by the generator process, it is possible to approximate very closely the composition of the vinegar which can be made from it.

BUREAU OF CHEMISTRY
U. S. DEPT. OF AGRICULTURE
WASHINGTON

ON THE DECREASE OF AVAILABLE PHOSPHORIC ACID IN MIXED FERTILIZERS CONTAINING ACID PHOSPHATE AND CYANAMID

By R. N. BRACKETT

Received July 25, 1913

About two years ago one of the fertilizer companies in this state found that one of their brands ran deficient in available phosphoric acid, although it was thought that ample provision had been made in overage for that ingredient. A representative of the company stated that calcium cyanamid had been used as one of the ingredients of his mixture. As this material usually contains an excess of free lime it appeared possible that the cause of the deficiency in available phosphoric acid in his goods might be traceable to the fact that the soluble or the reverted phosphoric acid had been to some extent converted into insoluble.

Preliminary experiments¹ on mixtures containing cyanamid showed that there was a slight decrease of available, due to the increase of the insoluble over that calculated for the mixture.

In the early spring of 1912 a mixer in a near-by town made up a mixture to analyze: 10 per cent available

phosphoric acid, 4 of ammonia and 4 of potash, using calcium cyanamid as one ingredient of his mixture. His formula was as follows:

	Pounds
Acid phosphate, 16 per cent.....	1250
Calcium cyanamid.....	200
Dried blood.....	250
Muriate of potash.....	175
1/2 and 1/2 mixture (composed of 1/2 16 per cent acid phosphate and 1/2 C. S. meal, damaged).....	125
	2000

Upon having this mixture analyzed in a commercial laboratory it was found to be deficient in available phosphoric acid. We received a sample through a purchaser, and also found it deficient in available phosphoric acid, analyzing about 8-4-4, instead of 10-4-4. At our request this mixer consented to send us samples of the materials above mentioned.

Before these materials were received, we made up a mixture¹ of an acid phosphate and cyanamid, using the proportions given above. The acid phosphate used gave as an average of six analyses:

	Per cent
Total phosphoric acid.....	18.37
Water-soluble phosphoric acid.....	13.58
Insoluble phosphoric acid.....	1.74

On a 0.3 gram sample, the cyanamid analyzed 14.97 per cent of nitrogen.

The mixture consisted of 250 grams of the acid phosphate and 40 grams of cyanamid, a ratio of one part of the cyanamid to 6.25 parts by weight of the acid phosphate; the initial temperature of the materials was 21° C. and upon mixing the temperature increased to 32° C.

RESULTS (ZERBST AND HUTSON)

	Phosphoric acid—Per cent			
	Total	Water-soluble	Insoluble	Available
Original acid phosphate.....	18.37	13.58	1.74	16.63
Analysis of the mixture, calculated, if no change on mixing....	15.84	11.71	1.50	14.34
Average of five analyses, 5 days after mixing.....	15.82	3.96	1.58	14.24
Average of three analyses, 12 days after mixing.....	...	3.54	1.69	14.13
Average of four analyses, 19 days after mixing.....	...	3.45	1.78	14.04
Average of six analyses, 26 days after mixing.....	2.28	13.54
Average of two analyses, 33 days after mixing.....	2.75	13.07
Average of three analyses, 40 days after mixing.....	3.21	12.61
Average of three analyses, 47 days after mixing.....	3.57	12.25
Work discontinued at end of 47 days.				

These results would appear to indicate that the conversion of the water-soluble or of the dicalcium phosphate to tricalcium is not simply a function of the temperature and of the alkalinity of the cyanamid, as is held by some, but that the element of time is perhaps of equal importance with the temperature. Hence it might well happen that a mixture freshly made up would show the required and desired amount of available, and yet be found deficient when analyzed some weeks later. The results of this experiment

¹ Made by L. D. Boone. Results not available.

¹ This work was done by G. H. Zerbst and H. M. Hutson.

indicate that it would be very interesting to continue the analyses until the water soluble had ceased to decrease and the insoluble to increase, and it is our hope to be able to take up this problem in the near future, working on a much larger scale.

On receipt of the above mentioned samples, a mixture was made of 3300 grams of the acid phosphate and 528 grams of the cyanamid, being a ratio of one part by weight of the cyanamid to 6.25 parts by weight of the acid phosphate; the materials were mixed in a glass jar; the initial temperature of the materials was 22° C.; upon mixing, the temperature rapidly increased to 52° C. As a mean of three analyses, the acid phosphate was found to have the following composition:

	Per cent
Total phosphoric acid.....	18.81
Insoluble phosphoric acid.....	0.34
Water-soluble phosphoric acid.....	16.98

RESULTS—(ZERBST AND HUTSON)

Phosphoric acid—Per cent

	Total	Water-Soluble	Insoluble	Available
Original acid phosphate.....	18.81	16.98	0.34	18.47
Analysis of mixture, calculated, if no change on mixing.....	16.21	14.64	0.29	15.92
Analysis of samples drawn within a few days after mixing, mean of 8 samples.....	16.17	1.91	1.35	14.82
Average of three samples drawn three weeks later.....	...	1.25	2.30	13.87

The work had to be discontinued at this point, as no more time was available for the men who had undertaken it. It is noteworthy that, while the water-soluble decreased only from 1.91 to 1.25 in three weeks, the insoluble increased from 1.35 to 2.30 per cent.

Last February, E. L. Hutchins, chemist to a near-by fertilizer plant, reported difficulty in making up a 10-4-4 mixture, using as one ingredient of his mixture calcium cyanamid. I regard this as the best instance of the danger of the decrease of the available phosphoric acid in mixtures in which cyanamid is used, which has come under my observation; and as an especially excellent illustration, as these experiments were conducted on a factory scale. With the permission of Mr. Hutchins, I give the following account of his experiments:

FORMULA USED

1250 pounds of 16 per cent acid phosphate
100 pounds of 10 per cent Kanona tankage
150 pounds of 11 per cent dried fish scrap
100 pounds of 16 per cent dried blood
150 pounds of 18 per cent cyanamid
52 pounds of 25 per cent sulphate of ammonia
140 pounds of 50 per cent muriate of potash
58 pounds of 18 per cent hard salts

2000

The acid phosphate actually analyzed:

	Per cent
Total phosphoric acid.....	17.24
Insoluble phosphoric acid.....	0.89
Available phosphoric acid.....	16.35

The above formula was made up as follows:

First day's run, January 20, 1913, amount made up 180 tons
 Second day's run, January 21, 1913, amount made up 171 tons
 Third day's run, January 22, 1913, amount made up 171 tons

Each of these runs was dumped into the same pile, sampled the same day and analyzed the next day. Samples were also taken the 24th and the 28th of January, and on the 5th of February, and these samples were analyzed with the following results:

		Phosphoric acid					
		Moisture	Total	Insoluble	Available	Ammonia	Potash
1.	Jan. 21, 1913....	11.22	11.67	1.68	9.99	4.12	4.76
2.	Jan. 22, 1913....	11.90	11.79	1.68	10.11	4.02	4.30
3.	Jan. 23, 1913....	11.66	11.65	1.80	9.85	4.13	4.38
4.	Jan. 24, 1913....	11.02	11.72	2.35	9.37	4.13	4.09
5.	Jan. 28, 1913....	10.48	11.70	2.99	8.71	4.21	4.31
6.	Feb. 5, 1913....	9.70	12.25	3.37	8.88	4.18	4.22

The sample analyzed January 28th was taken from the "face of the pile" and that of February 5th from the "base of the pile." Mr. Hutchins' attention was first attracted by the results of the analysis of January 24th, and he was led thereby to draw and analyze the other samples. It is evident from these results that in a mixed fertilizer containing acid phosphate and cyanamid in the ratio of one part of the latter to 8.33 of the former, there is an increase of the insoluble and a consequent decrease of the available phosphoric acid on standing, even a week or two; this change may cause the fertilizer to become deficient in available phosphoric acid.

Mr. Hutchins kindly furnished us with a considerable quantity of each of the materials used in his formula. Owing to some misunderstanding, the mixture was made up of one part of cyanamid to 9.8 parts of the acid phosphate. The rise of temperature was only six or eight degrees, but even with this ratio there was a gradual increase of the insoluble, as shown by the following results:

In the formula were used 6667.62 grams of acid phosphate and 680.11 grams of cyanamid, with the remainder of the ingredients in proportion.

RESULTS—(L. D. HUTSON AND J. F. KING)

Phosphoric acid—Per cent

	Total	Water-soluble	Insoluble	Available
Original acid phosphate.....	17.50	13.09	0.68	16.82
Calculated analysis of the mixture, made up March 1st, if no change on mixing.....	11.58	8.67	0.47	11.11
Analysis, sample drawn April 12, 1913.....	...	8.06	0.76	...
Analysis, sample drawn April 18, 1913.....	0.81	...
Analysis, sample drawn April 24, 1913.....	...	7.96	1.11	...
Analysis, sample drawn May 2, 1913.....	...	7.94	1.14	...
Analysis, sample drawn May 9, 1913.....	...	7.24

In addition to the facts above adduced, it may be interesting to state, as pointing in the same direction, that of the 70 samples of complete fertilizers found deficient in available phosphoric acid alone, during the past fertilizer season, seven were registered as having calcium cyanamid as one of their ingredients; eleven brands were not registered at all; and it is more than likely that cyanamid was an ingredient of many of the remaining 52 samples though the fact was not stated in the registration.

Acknowledgments are due Assistant Professor G. F. Lipscomb for his careful oversight of the work of the students; to the students themselves and to Mr. E. L. Hutchins for furnishing us with materials and for the use of his experiments and results.

CONCLUSIONS

I. From experiments conducted in this laboratory, it has been shown that when cyanamid is mixed with acid phosphate in the ratio of one part of the former to 6.25 or 8.33 or even 9.8 of the latter, there is, on standing, a gradual increase of the insoluble and consequent decrease of the available phosphoric acid in the mixture, and that this is true whether the mixture consists simply of the acid phosphate and cyanamid, or whether ammoniates and potash salts are also present.

II. The experience of at least three manufacturers working on a factory scale has shown that there is a decrease of the available phosphoric acid when calcium cyanamid and acid phosphate are used in mixed fertilizers in the ratio of one part of the former to 6.25 or 8.33 of the latter, thus confirming our own work done on a small scale.

III. The results of our fertilizer inspection analysis this past season point to the same fact; *i. e.*, that there is danger of falling off in the available phosphoric acid when calcium cyanamid and acid phosphate are used together as ingredients of a mixed fertilizer.

IV. The results of all these experiments indicate that the time element has an important influence in determining the increase of insoluble phosphoric acid, and must be considered in addition to the elements of temperature and the alkalinity of the cyanamid.

V. It appears from the facts given in this paper, that, though it may be said that the effect of mixing cyanamid with acid phosphate will not injure the fertilizer from the farmer's standpoint, the manufacturer must exercise some care as to the amount of the cyanamid used in a mixture, else his mixture may, upon inspection and analysis, be found deficient in available phosphoric acid.

CHEMICAL DEPARTMENT
CLEMSON AGRICULTURAL COLLEGE
SOUTH CAROLINA

LABORATORY AND PLANT

THE DESIGN OF AN EXPERIMENTAL WOOD DISTILLATION PLANT

By H. K. BENSON AND MARC DARRIN

Received August 18, 1913

The utilization of waste wood in the Pacific Northwest has recently attracted much attention. The interest lies partly in the necessity of clearing the logged off or "cut over" lands which now number over three million acres in the State of Washington alone. In a more popular sense, the interest, however, centers about the waste wood of the sawmills. In the latter it has been the practice to install wood burners or incinerators to dispose of the mill waste, and hundreds of cords of wood are thus destroyed daily. In the popular mind this waste is regarded as an economic crime, and several efforts have been made to establish a wood distillation industry in the Northwest, all of which have been commercial failures.

With a view to giving some assistance in solving this problem the University of Washington cooperated for some time with the Bureau of Plant Industry of the United States Department of Agriculture in land clearing studies and at the present time is in cooperation with the United States Forest Service in certain yield studies of distillation products from both Douglas fir stumps and the waste wood of sawmills operating in the western part of the State of Washington. After some years of experience with this problem, both from a theoretical standpoint and from practical participation in the industry, it appeared to the senior author of this paper that the failure of the commercial plants could, in each case, be traced to inferior and unusual methods of operation rather than to inferior products and lack of market as usually asserted. After personal visitation of the principal distillation plants in the

United States by both of us, we selected the type of plant described in this article as most nearly applicable to economical operation in the distillation of mill waste. The plant thus designed has been erected cooperatively by the United States Forest Service and the University of Washington and is now in operation. In this article only the design of the plant will be described since the results obtained will be the subject of later publications by the Forest Service.

The general layout of the plant is indicated by the legend descriptive of Plate 1. The wood for distillation is measured (4), weighed (3), placed in retort buggies (7), and distilled in the retort (21). The products of distillation are conducted from the retort through a bottom vapor outlet (25), into the tar separator (26), thence into the condenser (29), and finally the gases are stored in the gas holder (14), where they are sampled and measured and finally pass to the furnace (18) for combustion. For the estimation of the liquid products, the distillate is pumped (39) from the pyroigneous acid tank (30) into a feed tank (38), from whence it flows by gravity into a copper still (36) heated by steam coils. The resulting distillate is separated (40) into light oil and crude wood vinegar (containing acetic acid, methyl alcohol, acetone, etc.) and stored in tanks for sampling.

The main interest centers, however, in the design of the retort. For experimental purposes a capacity of one-half cord was determined upon, which required dimensions approximately 18 feet 1 inch long. The shell of the retort is 4 feet 1 inch wide and 3 feet 2 inches high, made of one-fourth inch steel and is covered on the outside to a thickness of two inches with standard heat insulation material. At one end a furnace is provided, the heat from which is conducted

through four iron flues of five inches diameter. These flues extend lengthwise within the retort as shown in a tight fit. The door is shut tightly by means of four cast iron eccentric clamps which act on two steel bars extending across the outer surface of the door.

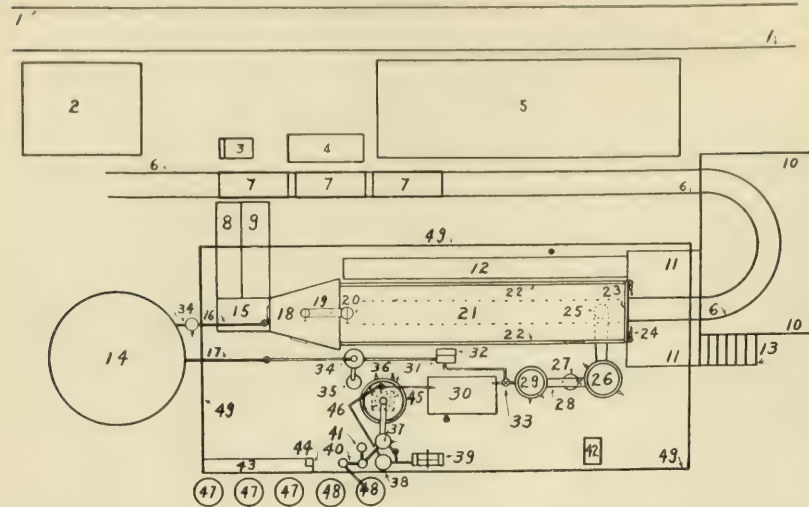


PLATE 1

- | | | |
|----------------------------|-----------------------------|-------------------------------|
| 1. Railway switch. | 18. Furnace. | 34. Back-fire traps. |
| 2. Charcoal yard. | 19. Flue by-pass. | 35. Gas tar tank. |
| 3. Platform scales. | 20. Stack. | 36. Refining still. |
| 4. Cord measure. | 21. Retort. | 37. Condenser. |
| 5. Wood yard. | 22. Heat insulation. | 38. Distillate feed tank. |
| 6. Retort buggy track. | 23. Retort door. | 39. Pump. |
| 7. Retort buggies. | 24. Door clamps. | 40. Oil separator. |
| 8. Charcoal chute. | 25. Bottom vapor outlet. | 41. Oil receiver. |
| 9. Wood chute. | 26. Tar separator. | 42. Crude alcohol tank. |
| 10. Retort buggy platform. | 27. Separator tar tank. | 43. Work table. |
| 11. Retort door platform. | 28. Pipe to condenser. | 44. Transformer and switch. |
| 12. Retort running board. | 29. Condenser. | 45. Sewage basin. |
| 13. Steps. | 30. Pyroligneous acid tank. | 46. Still tar tank. |
| 14. Gas storage tank. | 31. Gas booster. | 47. Tar tanks. |
| 15. Firing platform. | 32. Electric motor. | 48. Crude wood vinegar tanks. |
| 16. Gas pipe to furnace. | 33. Gas vent to air. | 49. Building. |

Plates 2 and 3, terminating in return bends at the back end of the retort. From thence they extend to the front end of the retort where they enter a smoke chamber, which in turn opens into the stack. The course of the heated gases of combustion is shown by the arrows in Plate 2.

The wood for distillation is piled vertically in three retort buggies with sides made of steel screening. The buggies operate on steel rails which contain a removable

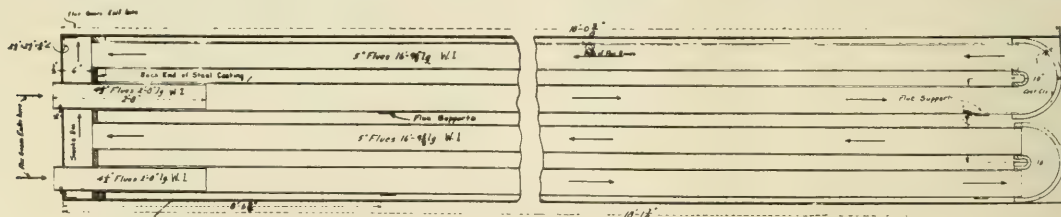


PLATE 2

section at the retort door, thus forming a continuous railway from the fore end of the retort to the wood yard and charcoal pile.

The retort door and door seat are made of cast steel and are carefully planed and milled so as to insure

and control of temperature. By thorough insulation of the retort shell, radiation losses from the shell are minimized, the temperature of the stack gases is more nearly that of the retort interior, the uniform distribution of heat prevents local overheating, and the retort suffers less depreciation due to unequal strains from high temperatures than in the case of retorts exposed to the direct scaling and buckling action of heat.

A number of considerations determined the selection

of a bottom vapor outlet. In the distillation of the coniferous woods it has been the writers' experience that coke deposits usually exist on charcoal drawn from the bottom of the retorts. It is generally assumed that such coke is the product of secondary distillation

of tar. In other words, when tar is in the process of formation from wood, it forms a high boiling volatile

planation has been verified by actual operation, coke being found on the charcoal only where oleo-resin or "pitch" had previously existed in the wood.

For the purpose of determining the size of flues the following assumptions were made:

- (1) The distillate has the same average properties as water.
- (2) Maximum distillate per cord, 300 gallons.
- (3) Radiation of insulation, 4.56 B. t. u. per sq. ft. per minute.
- (4) Radiation of exposed door, 24.54 B. t. u. per sq. ft. per minute.
- (5) Atmospheric temperature, 70° F.
- (6) Maximum temperature inside retort, 700° F.
- (7) Temperature of heating gases at entrance to flues, 1500° F.
- (8) Average temperature of heating gases upon leaving flues, 700° F.
- (9) Specific heat of retort steel and iron of buggies, 0.12.
- (10) Specific heat of wood, 0.650.
- (11) Maximum non-condensable gas per cord of wood, 10,000 cu. ft. weighing 0.08 pound per cu. ft.
- (12) Specific heat of non-condensable gas, 0.237.
- (13) Chemical reactions of an endothermic character balance those of an exothermic character.
- (14) Average radiation of flues, 3.63 B. t. u. per hour per sq. foot per degree F.
- (15) Average convection from flues, 1.06 B. t. u. per hour per sq. ft. per degree F.

With the further assumption that the time of distillation required 20 hours of firing, the total consumption of heat units was computed as shown on following page.

mixture with the lighter- and lower-boiling products resulting from the decomposition of wood. A slight cooling of the vapor causes a change in the concentration of the vapor's constituents and tar is precipitated in minute particles which are carried along mechanically. This, however, causes an increase in the density of the vapor and it tends to fall back into the retort. When it does this it becomes reheated, but instead of acting as it did at the time of its formation, it is now fractionally distilled, giving off various light oils and finally being decomposed with coke as the residue.

The bottom outlet should eliminate this possibility through active convection currents and distribution of heat within the retort. Thus the vapors rise on either side of the retort in the flue area between the outer side of the buggy and retort. The vapors there pass along the top, approaching from both sides a region near the top center, pass through the wood (which is piled vertically) in the buggies, and thence along the bottom of the buggy and retort to the vapor outlet, which is under a slightly diminished pressure due to the suction produced by the condenser or the fan. Should the tar for the reasons above given become liquefied, it flows by gravity into the vapor outlet and is not subject to redistillation. This ex-

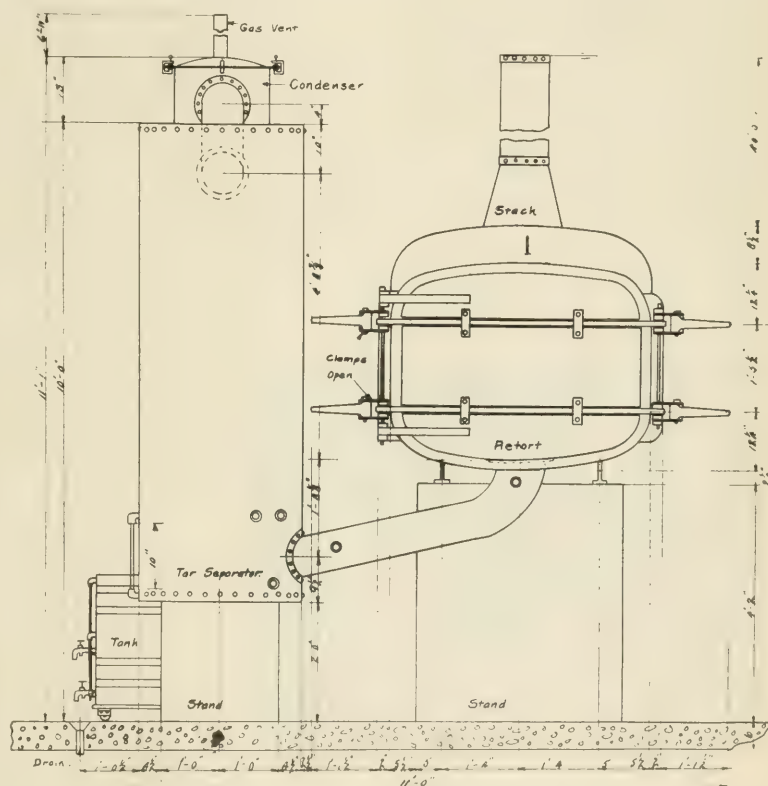


PLATE 4—FRONT VIEW. RETORT AND APPARATUS SET UP

To supply this heat, use was made of the following computation:

$Q = A(T - t)(r + c)$ where Q denotes heat sup-

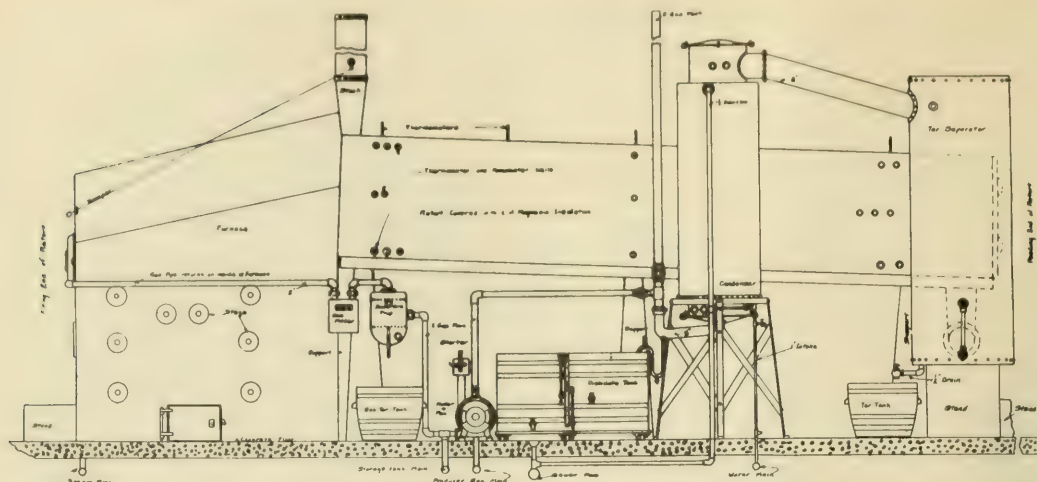


PLATE 5 SIDE VIEW. RETORT AND APPARATUS SET UP

TOTAL CONSUMPTION OF HEAT UNITS

	B. t. u.
(1) To heat and vaporize 150 gallons of distillate.....	1,430,000
(2) Radiation through insulation.....	1,512,000
(3) Radiation through exposed door.....	412,000
(4) To heat buggies and retort 600° F.....	990,000
(5) To heat wood 300° F.....	300,000
(6) Heat carried away by non-condensable gases.....	56,700
(7) Minor losses.....	100,000

Total heat lost in 20 hours..... 4,800,700

Total heat lost per hour (roughly)..... 250,000

plied; A , the total area of the flue surfaces; T , the average temperature of the gases within the flues; t , the average temperature within the retort; r , heat units given off by radiation; and c , heat units given off by convection. Hence,

$$Q = 0.416 \times 3.14 \times 16.6 \times 8 (1500 + 700 \cdot 2 - 700) \\ (3.63 + 1.06),$$

or 325,000 B. t. u. will be supplied per hour. Ac-

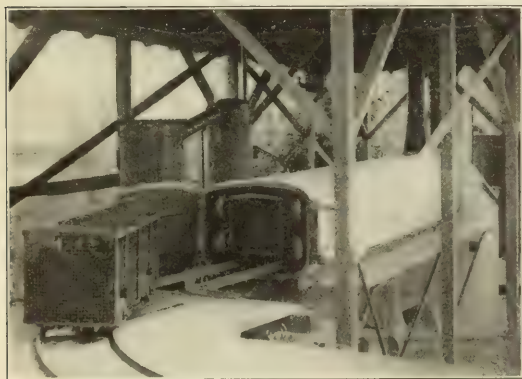


PLATE 6

cordingly by computation, the heat exchange is shown to be more than sufficient to produce distillation taking place under the conditions as above assumed, and this computation is verified by the results obtained in the

operation of the retort, which requires from 18 to 20 hours per run of three-eighths to one-half cord of wood.

In Plate 6 is given a general view of the plant as it appeared shortly after its installation.

LABORATORY OF INDUSTRIAL CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE

AN APPARATUS FOR DETERMINING THE MELTING POINTS OF SUBSTANCES OF INDEFINITE MELTING POINT

By A. P. BJERREGAARD

Received July 30, 1913

The determination of the true melting point of substances which do not melt sharply at a definite temperature but which gradually soften under the influence of heat and finally become soft enough to be liquid, is one of great difficulty. Indeed it can hardly be said that such substances have any true melting point. Ordinary coal tar pitch such as is used for roofing, etc., is an example of the class of substances under discussion here. As is well known this material at the ordinary atmospheric temperature when struck with a hammer flies to pieces like glass. Nevertheless, if a barrel of it stands for any length of time the pitch will slowly flow out of every crack and crevice or out of the open bung-hole just like a liquid. It may indeed be called a brittle liquid, and this class of substances might be called solid liquids. If coal tar pitch is warmed a little it gets softer and flows somewhat more rapidly; if it is further heated it becomes still softer and flows still more rapidly. Finally, when hot enough it can be made to flow nearly or quite instantaneously like water. When shall we say that coal tar pitch is melted?

Petroleum asphaltums prepared by oxidizing petroleum residuum also belong to this class of bodies, although their characteristics are somewhat different from those of coal tar pitch in that they are softer at ordinary temperatures and require higher temperatures to flow together when exposed for long periods of time to small degrees of heat. They also have a

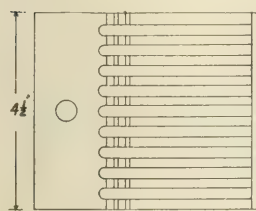
higher range of melting points as this term is understood in this article.

Experiment shows that an air-blown petroleum asphaltum which when heated rather rapidly becomes liquid at about $135^{\circ}\text{C}.$, will flow down an inclined plane upon which it may be placed at $40^{\circ}\text{C}.$ if kept at that temperature a long time, say 18 hours. Shall we say that this substance fuses at $40^{\circ}\text{C}.$ or at $135^{\circ}\text{C}.$?

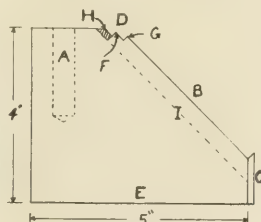
There appear to be two stages or two temperature points in this gradual softening, which may be of importance in the examination of these substances. *First*, there is that temperature point or approximate point, at which the firm solid or pseudo-solid material just begins to soften, so as to be slightly plastic, or so that if left a long time at that temperature it will flow and finally come to a level in its container. *Second*, there is a temperature at which the substance is so fluid that it can readily and quickly flow to a level in its containing vessel; in other words, it possesses the properties usually ascribed to liquids.

The apparatus now to be described is one for determining the temperature of this second kind of melting. It can scarcely be called a flow point apparatus, although the flow of the sample is measured.

It consists of a block of iron of suitable dimensions, with one face at an angle of 45° to the horizontal. This inclined face is provided with grooves, as further described below. The block is also provided with a small cistern to contain mercury in which is placed the thermometer for reading the temperature of the block. A useful size for this apparatus is about $4\frac{1}{2}$ inches wide, 4 inches high and about 5 inches long. This will contain 9 grooves of the size described below. A top view is shown in Fig. 1, and a side view in Fig. 2; here, *A* is the mercury



TOP
FIG. 1



SIDE
FIG. 2

cistern, *B* the inclined grooved face, *C* is a small stop arranged so that a sheet of glass, or transparent mica laid over the inclined face will be supported and prevented from sliding off, *D* is a series of step-like cuts made across the ribs between the grooves of the inclined face. The top cut *FH* is deeper than the second by one-eighth of an inch, the second cut *FG* is one-eighth of an inch deeper than the top of the ribs on the inclined surface. The length of the top cut is one-quarter of an inch from the angle *H* at the top, down to the step up *F* of the second cut; the length of the second cut is one-quarter of an inch from *F* to *G*.

The grooves are one-quarter inch wide, and their vertical sides are one-quarter inch deep to the beginning

of the curved bottom. The latter is of semicircular cross-section with a radius of one-eighth inch. The ribs may be $\frac{7}{32}$ inch thick. The dotted line *I* represents the bottom of the grooves.

For use, mercury is poured into the cistern *A*, which does not need to be very wide (say $\frac{1}{2}$ to $\frac{3}{4}$ inch) and the thermometer is inserted. The samples of material to be tested are pressed into the topmost parts of the grooves between *F* and *H* so as to fill the space which is shaded in Fig. 2. About 0.17 gram of asphaltum is needed for this. A sheet of glass or mica is laid on *B* (to shut off cold air drafts), and heat is applied at *E* by means of a Bunsen burner. Each sample will gradually soften and sag down the groove; when it is liquid enough to reach from *F*, its original lower boundary, to *G*, a distance of one-quarter inch, the thermometer reading is taken as the melting point. Marks may be made at intervals down *B*, say at every one-half inch and the behavior of the flowing material as it passes each in succession may be studied as to temperature and time differences.

It is important that the amount of material used in comparative trials should be sensibly the same. Otherwise the melting points observed will differ somewhat according to the relative sizes of the samples. Thus in two trials, certain specimens of air-blown petroleum asphaltum were applied in differently sized pieces and each series tested at the same time with the following results:

MELTING POINTS OF DIFFERENTLY SIZED PIECES OF PETROLEUM ASPHALTUM

Sample	No. 1	No. 1	No. 2
Rate of heating for $10^{\circ}\text{C}.$	77 sec.	100 sec.	100 sec.
Small piece.....	$184^{\circ}\text{C}.$	$181^{\circ}\text{C}.$	$183^{\circ}\text{C}.$
Medium piece.....	$180^{\circ}\text{C}.$	$175^{\circ}\text{C}.$	$178^{\circ}\text{C}.$
Large piece.....	$178^{\circ}\text{C}.$	$171^{\circ}\text{C}.$	$174^{\circ}\text{C}.$

It will be seen that sample No. 1 showed in one case a difference of $6^{\circ}\text{C}.$ in melting point and in the other case of $10^{\circ}\text{C}.$, depending on whether a large or a small piece was used. The large piece of No. 1 used at rate 77 sec. was not the same in size as that used in rate 100 sec.; the same remark applies to the medium and small pieces. The large pieces were about the size of peas, the small pieces about one-third this size.

In order to overcome this cause of discrepancy the space in the upper part of the groove should, as already said, be filled with the material to be tested, and then the top scraped off even with the surface of the partly cut off rib. By this means sensibly the same sized sample may always be subjected to test, thereby eliminating one of the uncertainties of the melting point of the substances under consideration.

The reason that a larger piece appears to fuse at a lower temperature than a smaller piece seems to be that the action of gravity is relatively greater at the same time that the action of capillarity is relatively less, with the larger piece. The first force tends to pull the mass down the incline, and so to render the apparent melting point lower. The second force tends to prevent the liquefied, or semi-liquefied sample from flowing down and, therefore, to render the apparent melting point higher. These circumstances

necessarily operate in most other methods of determining the melting point of the classes of bodies under consideration. But in this apparatus the variations can be controlled by exactly filling the space as described, whereas in most other methods no such control is as easily obtainable.

As has already been stated material of indefinite melting point will flow at low temperatures if given time enough. Time is therefore an important factor in this determination and must be taken into account.

That the temperature at which substances of indefinite melting point actually fuse depends considerably on the rate of heating is illustrated by the following table:

MELTING POINTS OF AIR-BLOWN PETROLEUM ASPHALTUM FOR DIFFERENT RATES OF HEATING						
Rate for 10° C. 43 sec.	65 sec.	68 sec.	75 sec.	113 sec.	126 sec.	
Sample No. 1	119° C.	114° C.	114° C.	115° C.	...	112° C.
2	140	134	133	135	128° C.	128
3	157	154	150	149	147	147
4	161	160	156	156	151	150
5	...	170	169	166	157	...

It follows, if comparable results are desired, that the heating up must be conducted at a given rate.

For many purposes, however, where simply relative results are desired, there is no need of heating at a definite rate with this apparatus provided only that the rate of heating is comparatively uniform.

For such relative determinations the several samples to be compared are pressed into the grooves as described, and the several melting points observed are read and compared. Even very slight differences of melting point can be observed in this way.

A rate of about 100 seconds for a rise of 10° C. is the most convenient for use with an apparatus of the size already described. This rate is readily obtained with a good sized Bunsen burner burning so that the flame impinging on the bottom of the block forms a circular disk of about 3½ inches in diameter—at least that is the size with the pressure of artificial gas in the city of Cleveland.

All methods heretofore proposed, so far as I am aware, for determining the melting points of substances of indefinite melting point are also subject to some rate of heating factor. This rate is controlled with great ease in the method here described, and may be entirely neglected with this apparatus under the conditions mentioned above.

The rate of heating is without influence on the temperature at which substances of sharp melting point fuse in this apparatus. For example a certain sample of commercial stearic acid, which fused quite sharply at 59¾° C. by the usual capillary tube method, fused by the iron block method at 59¾° C. when heated 10° C. in 125 seconds, and at 60° C. when heated 10° C. in 50 seconds. This last rate is about the fastest; it is feasible to use by this method. Substances of sharp melting point do not gradually sag down the incline as the heating progresses. They remain entirely unchanged until the temperature reaches the melting point, and then they suddenly fuse and flow down the inclined groove quite rapidly.

Hence, for determining the melting points of sub-

stances of sharp melting point for commercial purposes this apparatus will be found of great use.

Lastly, in at least some cases, the melting point of substances of indefinite melting point is influenced by the amount of working or kneading to which the sample has been subjected. This is exemplified by the following figures; the rate of heating was 10° C. in 77 seconds:

MELTING POINTS OF AIR-BLOWN PETROLEUM ASPHALTUM		
	Not kneaded	Well kneaded
Small piece.....	170° C.	167° C.
Large piece.....	167° C.	160° C.

Here the kneading has lowered the melting point from 3° to 7° C. This is the most difficult condition to control in the samples submitted to test, because it is impossible to avoid some kneading in pressing the sample into the slot of the machine. The best way to overcome it, and to secure comparable results, is to thoroughly knead each pellet of the samples before pressing them into the slots. Here again the same factor of kneading enters into all methods heretofore proposed for determining the melting points of this class of substances.

As above stated all these conditions operate to cause variations in melting point in every form of apparatus heretofore proposed. But in none of them, so far as the author has tried them, is it possible to satisfactorily overcome the inaccuracies and variations caused by the peculiarities in behavior of these materials of indefinite melting point. But by means of the proper use of the apparatus herein described it has been possible to attain accuracy of results entirely unattainable before this apparatus was put into use.

During the two years in which this apparatus has been in use in this laboratory, the author has found it of great value for lubricating greases of every kind, for pitches, asphaltums, solid insulating compounds, and, in short, for every kind of substance whose melting point is lower than the boiling point of mercury and whose range of fusion is too wide for obtaining definite results by the capillary tube method. For such materials it appears to be as generally useful as the capillary tube is for those of sharp melting point.

The samples are quickly inserted into the slots, it takes but a short time to heat up to the melting point, the temperature is easily and accurately read, many samples can be tested at once, and the apparatus is easily cleaned.

The best way of cleaning this melting-point block is to immerse it while still warm into a can of liquid which is a solvent for the substance tested, for example naphtha, if petroleum pitch or lubricating grease is in the apparatus. After a short soaking the samples can usually readily be scraped or wiped out, and then the slots are easily washed with a small piece of cotton waste or other rag. After that it is rinsed with clean naphtha and allowed to dry, when it is ready for use.

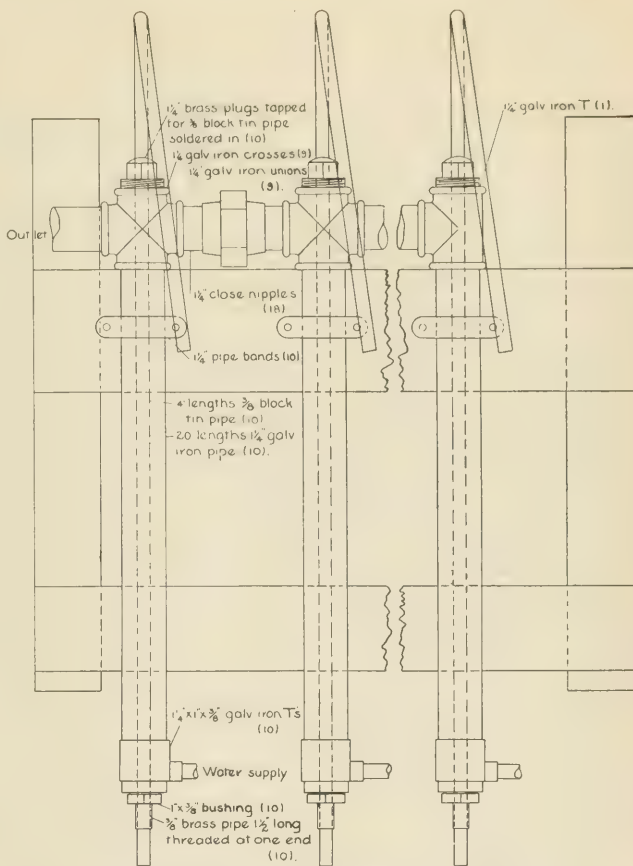
A MODIFIED BANK OF AMMONIA STILLs

By FRED BERRY AND L. H. VAN BUSKIRK

Received September 2, 1913

No doubt a majority of those in charge of laboratories where ammonia determinations are made, have been confronted, at one time or another, with the problem of designing or choosing some form of apparatus to be used for such determinations. Just such a problem had to be solved by the writers last year when plans were prepared for moving our laboratory into new quarters. The old bank of stills which had been in use here for many years had one large tank used as a condenser for the eight stills and the lower ends of the block-tin pipes were so located that one had to reach under a framework supporting the burners and flasks in order to replace or remove the nessler jars. This apparatus was in many respects far from satisfactory, but for one reason or another had not been replaced by a more convenient type.

When the necessity for such a change arose we were unable to secure much help in the way of drawings, specifications, etc., from other laboratories. We did, however, receive a photograph of an apparatus, of which this is a modification, but found some difficulty in estimating dimensions, etc., from a photograph alone. It occurred to the writers, therefore, that detailed specifications and drawings of this apparatus would be of great assistance to other workers who might care to duplicate it or construct a modification of it. While no claim is made for originality of principle, we do believe



FRONT VIEW FROM ABOVE THE LEVEL OF THE TABLE TOP

that some of the improvements added to former types are of distinct advantage and worthy of note.

The distinguishing points of this apparatus, in common with others of similar style, when compared with the majority of other forms are:

1. Unit construction, *i. e.*, each still has an individual condenser.

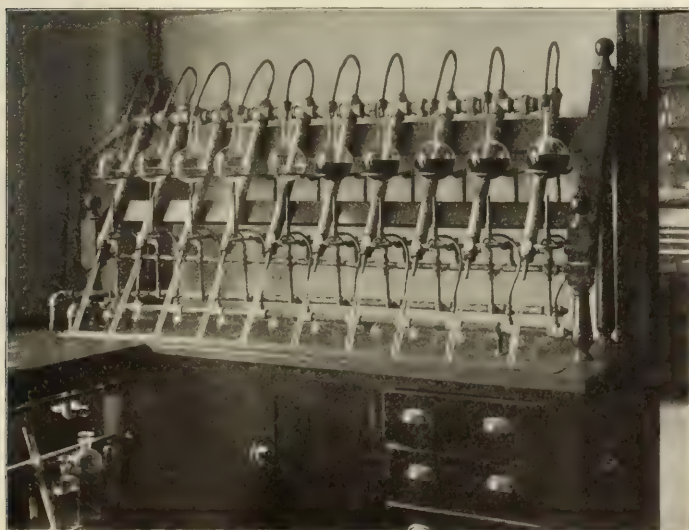
This means:

(a) Repairs can be made on one unit while others are in operation.

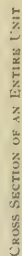
(b) Additional units can be added without much extra cost or trouble.

2. The distinguishing features of this type alone are:

(a) All ring supports for flasks and burners are attached to standards in the rear of the condensers, thus allowing free access to the flasks. The advantage of this will be apparent to those who have worked with the style where the uprights for the support of the flask rings projected above and were in front of the flasks.



PHOTOGRAPH OF ENTIRE APPARATUS ON LABORATORY BENCH



FRONT ELEVATION

(b) The block-tin pipes are soldered into brass nipples at the lower end and into brass plugs at the upper end of the condensers. This provides a perfectly

tight joint and gives a certain amount of rigidity to the lower end of the tin pipes.

OHIO STATE BOARD OF HEALTH
COLUMBUS, OHIO

ADDRESSES

OUR RADIUM RESOURCES¹

By CHARLES L. PARSONS²

The "wonders of radium," both fact and fable, have been treated so extensively in the scientific and public press that it is not my intention, nor is it at all necessary to repeat them here. Rather it is my wish to-day to present to a body of men interested in the development of American mining the present commercial situation as regards radium and its ores, and to point out, so far as I may, some of those future developments that already begin to be more or less distinctly visible.

A bulletin on the radium, uranium and vanadium situation, by R. B. Moore, physical chemist in charge of the Denver office of the Bureau of Mines, and K. L. Kithil, mineral technologist of the Bureau, will appear within a few weeks and will contain much detail of interest to the mining industry. Last April an advance statement, authorized by the Director, regarding this bulletin, brought out particularly the fact that practically all of the carnotite ore mined in the world in 1912 was shipped abroad and that this country was furnishing annually nearly three times as much radium from its Colorado carnotite deposits as all the rest of the world put together. It was further pointed out that this material has been bought by European buyers at a price entirely incommensurate with its radium value and that efforts should be made to keep at home both the radium itself and the profits of its manufacture; also that too much stress could not be laid upon the extensive waste of valuable radium ore thrown on the dumps of mines and prospects—much of it under such conditions that it could never be recovered.

The publication of this statement has already resulted in an increase of at least 33 per cent in the price of carnotite ore, and European buyers are awakening to the fact that they must pay to the American miner a price nearer the actual value of his ore. Also, a much lower grade of ore is now marketable, for whereas six months ago ore containing 2 per cent uranium oxide was the lowest grade accepted by European buyers, agents of these buyers are now asking for and actually purchasing ore containing no more than half this content of uranium. Furthermore, the operators are taking more care in separating their low-grade ore from the gangue and in protecting it from wind and weather. Moreover, old dumps are being sold and ore that a few months ago was thrown aside as valueless will be recovered from them.

In this paper I shall refer to other facts contained in this bulletin and shall mention some new developments having a direct bearing upon the American radium industry which have taken place since the manuscript was sent to the printer.

As is well known to all of you, the popular belief has been that the chief source of radium is the mineral pitchblende, especially that obtained from the mines now under the control of the Austrian government at Joachimsthal, Bohemia, and pitchblende is the richest and most eagerly sought uranium radium ore. Outside of the ore in Austria, the only pitchblende deposits of any size are those in Gilpin County, Colorado, from which some 30 tons more or less have been procured since the mineral became valuable as a source of radium. The Denver papers recently announced that these pitchblende-bearing mines have been acquired by Alfred I. duPont of Wilmington, Delaware, and it is greatly to be hoped that their exploitation under his direction

will yield an increased supply of this valuable mineral. It is not, however, so generally recognized that the mineral carnotite, which outside of the United States occurs only in low-grade ores mixed with ilmenite in the Olay district of South Australia and as a calcium carnotite (communicated by W. F. Hillebrand) under the name of Tyuyamyunite in Ferghana, Russian Turkestan, is by far the more important source of radium. From the most authentic sources it can be definitely stated that the Australian and Russian deposits do not compare in extent or richness with our own. The American carnotite is accordingly the largest source of radium at the present time and at least four times as much radium was mined in America in the form of carnotite in 1912 as has been produced from Colorado pitchblende since it was first discovered in that State.

Outside of carnotite and pitchblende, the only other known source of radium is the mineral autunite. The autunite deposits of Portugal have probably furnished a few milligrams of radium to commerce, and from the Mt. Painter deposits in South Australia a few tons of autunite-bearing ores have been shipped to London.

American carnotite is found chiefly in Montrose and San Miguel counties, Colorado, and in Utah northwest of these counties. The Utah deposits are at Green River, Table Mountain, Richardson, Fruita, Moab, and some 16 miles southeast of Thompsons. The ores of these deposits are of a lower grade than those of the Paradox Valley, but they are nearer to the railroads and transportation costs are much less. The Green River deposits have apparently become regular producers. In Colorado, prospects have been opened at Coal Creek, 14 miles north of Meeker and at Skull Creek 65 miles west of Meeker; but the richest of all American carnotite localities and indeed the richest known radium-bearing region in the world is that of the Paradox Valley, Colorado, extending from Hydraulic on the north to the McIntyre district on the south.

Geologists are now in the field making a special study of these carnotite ores with special reference to their occurrence and origin, of which altogether too little is now known. In the Paradox region the deposits seem to lie invariably just above the fine-grained La Plata sandstone. This rock is usually exposed high on the sides of the canyons, some of which are excelled in extent and in natural beauty by only the Grand Canyon itself. In a few instances, as at Long Park and Club Ranch, the deposits are only a few feet under the surface, the higher formations having been eroded; but for the main part, the stratum in which the carnotite occurs, when not entirely eroded, is deep below the surface of the mesa. Accordingly prospecting is mainly carried on along the sides of the canyons, and where vanadium and uranium stains are seen upon the rock the prospector blasts his tunnel in the hope of developing a pocket of the ore. The fact that the ore occurs in pockets renders prospecting uncertain, and there appears to be no present hope of insuring a successful search for pockets that are not exposed or do not happen to be near the surface. Although it is probable that many other pockets of carnotite occur at the same geologic horizon, their discovery, except where the ore-bearing stratum has been exposed by erosion, appears at present to be an almost hopeless task. The eroded sides of the canyons have been prospected again and again but new claims are still being opened and are being sold by the prospector to the larger companies or operators who mine the ore. In such a sale the prospector

¹ Paper presented before the American Mining Congress, Philadelphia, October 23, by permission of the Director of the U. S. Bureau of Mines.

² Chief of the Division of Mineral Technology, Bureau of Mines.

and the purchaser both take a decided risk, for at present no method is used to determine the extent of the ore in the pocket other than the "prospector's hole."

As few of the prospectors of the west are acquainted with carnotite and pitchblende, the following description of the ores has been issued from the Denver office of the Bureau of Mines and is sent to all who make inquiry:

"In reply to your letter for information concerning radium ores, the following facts may be of interest:

"Radium is found associated with uranium minerals only. Wherever uranium exists, radium is also found in the mineral; and where there is no uranium, radium has never been found. Uranium and therefore radium are found in this country in carnotite and its associated minerals, and in pitchblende. Carnotite is a lemon-yellow mineral usually found in pockets in sandstone deposits. The mineral may be in the form of light yellow specks disseminated through the sandstone, or as yellow incrustations in the cracks of the sandstone, or may be more or less massive, associated with blue, black, or brown vanadium ores.

"Pitchblende is a hard, blue-black ore that looks something like magnetite, but is heavier. It is found in pockets and veins in igneous rocks. This mineral is not nearly as widely distributed as carnotite. Occasionally it is found associated with an orange mineral called gummite.

"The best way to test these ores is to wrap, in the dark, a photographic plate in two thicknesses of black paper. On the paper lay a key and then, just above the key, suspend two or three ounces of the ore, and place the whole in a light-tight box. Pressure of the ore on the key and plate should be avoided. After three or four days, develop the plate in the ordinary way; and if the ore is appreciably radioactive, an image of the key will be found on the plate.

"The U. S. Bureau of Mines, 502 Foster Building, Denver, Colorado, will be glad to receive any samples of ores giving promise of containing radium and associated rare minerals, as indicated by the test above described. Though it cannot undertake to make chemical analyses or assays of such minerals for private parties, it will indicate the advisability of further examination."

The Colorado carnotite deposits were apparently first noted as far back as 1881, when Andrew J. Talbert mined some of the ore and sent it to Leadville where it was reported as carrying \$5 in gold per ton. This must have been an unusual ore as the carnotite now found does not carry the precious metal. In 1896, Gordon Kimball and Thomas Logan sent specimens to the Smithsonian Institution, Washington, D. C., and were informed that the minerals contained uranium. Shortly thereafter they mined 10 tons of ore, shipped it to Denver, and sold it for \$2,700 on account of its uranium content. Three years later, in 1899, Poulot and Voilleque collected and sent to France specimens which were examined by Friedel and Cumonge who recognized the existence of a new mineral and named it "Carnotite" in honor of M. Carnot then President of the French Republic. In 1900, Poulot and Voilleque leached carnotite ores at Cashin in the Paradox Valley to extract the uranium. They shortly after completed a small mill in the McIntyre district south of the Paradox and in this project had the cooperation of James McBride, a mining engineer of Burton, Michigan. Their mill ran until 1902 and during that time produced 15,000 pounds of uranium oxide. The mill was started again in 1903 by the Western Refining Company but ran only a year. Up to 1904, the mills appear to have been run wholly with the idea of obtaining the uranium and vanadium from the ore for no radium was extracted. Shortly afterwards the Dolores Refining Company built a new mill a short distance from the old one but after running for some years, this mill, too, shut down. In 1912, the American Rare Metals Company acquired the mill of the Dolores Refining Company and is now operating it, with the

special purpose of obtaining radium from the ores. The first attempt to extract radium in this country appears to have been made by the Rare Metals Reduction Company, under the management of Stephen T. Lockwood of Buffalo, N. Y. In September, 1900, Mr. Lockwood brought back from Richardson, Utah, samples of carnotite ore and in 1902 he published (*Eng. Min. Jour.*, of September 27th) the first radiographic plate from products of American carnotite. In June, 1902, he received 500 pounds of specially picked high-grade ore from Richardson, Utah, and in May, 1903, as a result of experimental work on this ore, he incorporated what was probably the first American company to operate a plant to produce radium as one of its products. In October, 1903, the first experimental plant was constructed and in April, 1904, the first 17-ton car of ore reached Buffalo from Richardson, Utah. The company obtained a fair percentage of extraction but the ore proved to be too low-grade and the Richardson deposits were abandoned. No radium in concentrated form was put upon the market, although barium sulfate concentrates were produced.

The General Vanadium Company which, with the Radium Extraction Company, is a subsidiary of the International Vanadium Company of Liverpool, England, was formed in 1909 and began work in 1910, the same year that the Standard Chemical Company of Pittsburgh, Pa., entered the field. Since that time these two companies have been engaged in mining carnotite. The ores from the General Vanadium Company have been shipped almost entirely abroad, while the Standard Chemical Company has shipped several hundreds of tons of carnotite to its works at Canonsburg, Pa. While it was stated at the time of the advance announcement of the bulletin to be issued by the Bureau of Mines that one American Company had actively entered into the production of radium no actual sale of American-produced radium could be authenticated. Since that time, however, the Standard Chemical Company has entered the American markets.

Besides the American Rare Metals Company and the Standard Chemical Company, a third company—the Radium Company of America with mines near Green River, Utah—has undertaken the production of radium in its plant at Sellersville, Pa. There is, therefore, every reason to hope that more and more of our ores will be worked up at home.

Besides the companies already mentioned, a number of independent operators mine and ship carnotite from the Paradox region and for the main part send their ores to Hamburg. Among the more prominent of these may be mentioned:

T. V. Curran, Placerville, Colo.

W. L. Cummings, Placerville, Colo.

O. B. Wilsmarth, Montrose, Colo.

David Taylor, Salt Lake City, Utah.

The costs of mining and especially of transportation are an important factor in the marketing of carnotite. The Green River deposits have a distinct advantage over the Colorado deposits in this respect, as they are nearer the railroad, but, as their ores do not average so high in uranium, this advantage is more apparent than real. The present costs of mining, sorting and sacking in the Paradox apparently vary from about \$28 to \$40 per ton. To this must be added an \$18 to \$20 hauling charge to Placerville, and, in most instances, an additional charge for burros from the mines to points that can be reached by wagon. The freight rate from Placerville to Hamburg via Galveston is \$14.50 per ton, so that the average cost at present to the miner of laying down his ore at the European markets approximates \$70 per ton. The selling price varies with the uranium content but is by no means proportional thereto, since a premium is always paid for rich ores. Very recently, however, a decided improvement has taken place and for 2 per cent ore, the price is now around \$2.50 per pound for the contained uranium oxide with an allowance of about 13 cents per pound for the vanadium

oxide content, so that the 2 per cent ore will now bring in Hamburg about \$95 per ton. One per cent ore is now salable but unless this ore is taken from the dump, so that the mining cost may be disregarded, it will scarcely bear present transportation charges from the Paradox, although it is more than probable that it will soon be shipped regularly from the Utah field.

A price of \$95 at Hamburg for 2 per cent ore leaves a fair margin of profit to the miner, as mining profits go, but when it is considered that this price represents only a little over one-sixth of the value of the radium content of the ore and that from this fraction of the value the American miner has to meet the outlay represented by the investment, by mining costs, transportation and assay costs and by losses in transit, it seems scarcely just that nearly five-sixths of the value should go to foreign manufacturers of radium, especially when the fact is considered that radium can be produced much more readily from carnotite than from pitchblende. There are two ways of reducing this difference between the actual value of the ore and the price that the miner receives. One is to hold our American ores for a higher price, and the second is to manufacture radium at home.

Large wastes are still taking place in the mining of carnotite, owing to the inability of the low-grade ores to bear transportation charges. As has already been pointed out, however, a distinct improvement in this respect has taken place within the last few months. The miners are beginning to realize the value of their old dumps and are attempting to save the low-grade non-shipment ore in such ways as will render its marketing possible when prices advance. The Bureau of Mines has done everything it can to impress the necessity of this truest kind of conservation upon the mine operator.

In addition there is prospect that most of the low-grade ores can be successfully concentrated by mechanical methods, and experiments at the Denver office of the Bureau of Mines indicate that a concentration of four to one can be obtained. In this concentration, however, there are losses which could be prevented by chemical concentration, but at the present time it costs more to ship the necessary chemicals to the mines than it does to ship the ores to places where these chemicals can be cheaply obtained. It would appear, however, that mechanical concentration can save at least one-half of the material that is now going to waste.

Although, until recently, the manufacture of radium from carnotite has been carried on almost wholly in France and Germany, there appears to be no good reason why our American carnotite should not be treated at home. Carnotite is much more easily treated than pitchblende and the essential features of methods for its chemical treatment are well known, although much of the mechanical detail of operation has been kept secret. As the mechanical requirements, however, are those which any well-grounded chemical engineer should be able to solve, there seems to be no good reason why any of our carnotite ores should be shipped abroad, even at two or three times the present market price of the material. As before stated, the essential features of chemical methods of extracting radium from its ores are well known. As regards the principles involved, the methods have advanced little beyond the original method published by Debiere.

The methods for carnotite may be described best in the words of Soddy, in an extract from "The Chemistry of the Radio Elements" by Frederick Soddy, page 45, published in 1911 by Longmans, Green & Co.

"The most important operations in the working up of radium-containing materials are the solution of the materials, consisting usually of insoluble sulfates, and the separation of the halogen salts of the alkaline-earth group in a pure state, followed by their fractional crystallization. The first operation is usually effected by vigorous boiling with sodium carbonate solution, filtering and washing free from sulfate. This is the well-known reaction

studied dynamically by Guldberg and Waage, whereby an equilibrium is attained between the two pairs of soluble and insoluble sulfates and carbonates. Naturally the greater the excess of sodium carbonate the larger the proportion of insoluble sulfate converted into insoluble carbonate. In this operation it is advisable not to wash at once with water but with sodium carbonate solution until most of the sulfates are removed, as thereby the reconversion of the carbonates back into insoluble sulfates is largely prevented. In dealing with crude materials, for example, the radium-containing residues from pitchblende, it is often advantageous to precede this operation by a similar one, using a sodium hydrate solution containing a little carbonate which dissolves part of the lead and silica present. The carbonates washed free from sulfates are treated with pure hydrochloric acid which dissolves the alkaline earths including radium. From the solution the latter may be precipitated as sulfates by sulfuric acid and reconverted back into carbonates as before. Or sometimes more conveniently they may be precipitated directly as chlorides by saturating the solution with hydrogen chloride: this is a very elegant method of great utility in the laboratory, for the most probable impurities, chlorides of lead, iron, calcium, etc., remain in solution and only the barium and radium chlorides are precipitated, practically in the pure state, ready for fractionation."

The price of radium appears for some time to have been holding steady at about \$120 per milligram of radium metal. This does not mean that the material is bought in the elementary condition but that the radium chloride and radium bromide, which are on the market, are paid for on the basis of the metallic radium they contain. This method of payment is a distinct advance over the old method of paying the same price indiscriminately for the chloride or bromide. This price of \$120 per milligram of the metal is equivalent to approximately \$91,000 per gram of radium chloride (RaCl_2), or \$70,000 per gram of anhydrous radium bromide (RaBr_2). Whether this price will rise, fall, or remain stationary can not be predicted. There is no question that there is to be an increased radium production and that meso-thorium is also coming upon the markets in increasing quantity but the uses of and demand for radium are apparently developing at an even greater rate. Furthermore, the supply of the material is limited and no large resources are in sight. Only one estimate has been published of the total quantity of radium in the Colorado carnotite deposits and that was 900 grams. This estimate is at least five times as large as has been made by any employee of the Bureau of Mines, reckoning all known deposits in the whole American field, even including material too low grade to be marketable. Besides the radium, the uranium and the vanadium present in carnotite are available assets, and recent developments indicate that all the uranium produced will soon be readily sold, while it is well known that there is a ready market for vanadium for vanadium steel.

The value to the public of these deposits is, however, not to be measured in dollars and cents. The value of the radium output of America will never compare with that of several of our common metals. The total value of the radium in the world's output of radium ores in 1912 was little more than \$1,000,000. Accordingly the value must ever be reckoned in what it can accomplish for the public knowledge and the public weal. No certain prediction can be made of the ultimate value of radium or of its possible applications to science or medicine, but enough has been done to show that radium is worthy of the fullest investigation by our highest scientific and medical authorities. Developments in its application to medicine are coming fast. The foreign medical press contains many apparently authentic reports of cures by its use. Interesting developments are also under way in America, and those who have had the largest personal experience in its use are most enthusiastic over its

future application. The public may soon look to important publications from leading American authorities who have had real experience in radium therapy. It is to be greatly regretted that owing to the high price of the material, only three or four American surgeons have, so far as the Bureau of Mines is informed, been able to use it in quantities sufficient for the drawing of decisive conclusions. In the progress of the future applications of radium to the curing of disease, nothing is more to be feared than its use in nostrums of every kind. The "wonders of radium" have been so extensively exploited in the public press that already the name is being employed as a psychological agent in advertisements of all kinds of materials, many of which contain no radium at all or, if this element is indeed present, in such small quantities that no therapeutic value can be expected. As bearing on the need of further experiment, attention is called to the fact that the concentrated action of large quantities of radium may effect cures that have been impossible with the smaller amounts heretofore available to the medical profession. It is doubtful if there is at the present time in the hands of the medical profession of America more than a single gram of this rare element, and the results of investigations soon to be published will show that the concentrated action of the gamma rays from several hundred milligrams arrest certain forms of cancer and other malignant growths when smaller quantities are without beneficial effect. It is highly important that the medical profession should also have some guarantee of the material they purchase even if it is purchased in small quantities, and I am glad to note that the U. S. Bureau of Standards is preparing to standardize radium preparations. As several frauds in the sale of radium have already been perpetrated upon American physicians, they should all require that the quality of the material purchased should be certified under conditions which prevent error.

In closing, I take pleasure in saying that I am authorized by the Director of the Bureau of Mines to announce that a co-operative agreement has been entered into with the newly organized National Radium Institute, whereby the Bureau obtains the opportunity of a scientific and technological study of the mining and concentrating of carnotite ores and of the most efficient methods of obtaining radium, vanadium, and uranium therefrom, with a view to increased efficiency of production and the prevention of waste.

The National Radium Institute was recently incorporated with the following officers:

HOWARD A. KELLY of Baltimore, *President*.

CURTIS F. BURNAM of Baltimore, *Vice-Prest.*

ARCHIBALD DOUGLAS of New York, *Secretary and Treasurer*.

JAMES DOUGLAS of New York and E. J. MALONEY of Wilmington, *additional Directors*.

The Institute has no connection with the mining of pitchblende, details of which recently appeared in the Denver papers. It has, however, obtained the right to mine 27 claims in the Paradox Valley region among which are some of the best mines in this richest radium-bearing region of the world. Nearly 100 tons of high-grade carnotite have already been procured. Under the agreement with the Bureau of Mines the technical operations of the mines and mill are to be guided by the scientific staff of the Bureau. Work will begin in an experimental plant to be erected in Colorado, using entirely new methods developed at the Denver office of the Bureau of Mines. Concentration experiments also will be conducted in the Paradox, probably at the Long Park claims, and if successful will be applied to reducing the wastes that now take place. Within a year at most the mill operations should make results certain and the extraction of ore and production of radium will then be continued on a larger scale. The separation of uranium and vanadium will also be studied, a contract having already been signed for all of these by-products that may be produced. All processes,

details of apparatus and plant, and general information gained will be published for the benefit of the people.

The Institute is supplied with sufficient funds to carry out its plans. The Institute has been formed for the special purpose of procuring enough radium to conduct extensive experiments in radium therapy with special reference to the curing of cancer. It also expects to carry on investigations regarding the physical characteristics and chemical effects of radium rays and it hopes, in time, to be able to assist or perhaps even duplicate the effects of these rays by physical means.

Actual experience, especially of the Institute's president, in the application of the 650 milligrams of radium and 100 milligrams of meso-thorium already in his possession, has led him and his associates to believe that with larger supplies many of the variables that cannot now be controlled may be fully correlated, and that radium may become the most effective agent for the treatment of cancer and certain other malignant diseases. Important results have already been obtained by using high concentration of the gamma rays of radium with the alpha rays entirely cut off and the beta rays largely eliminated. Hospital facilities in both Baltimore and New York are already supplied.

The activities of the Institute are sure to be of benefit to the prospector and miner by providing a greater demand for his already rare ore; to the plant operator by developing methods and by creating a larger market for his product; and to the people by assisting, and possibly by succeeding, in controlling the most malignant of diseases. The radium produced is intended for the Institute's own use and will consequently remain at home.

The Bureau of Mines is especially fortunate in this opportunity to coöperate in the technological features of the work of the National Radium Institute.

BUREAU OF MINES, WASHINGTON

THE RELATION OF BIG BUSINESS TO INDUSTRIAL PROSPERITY WITH SPECIAL REFERENCE TO MINING¹

By CHARLES R. VAN HISE²

In an address before the American Mining Congress on the above subject, the speaker, one of the leading political economists of the country, declared that the Sherman anti-trust act was responsible for the tremendous waste in mining through permitting unrestrained competition. He said that when the Sherman act was passed, "immediately the wheels, so far as coöperation was concerned, were turned back to the conditions of the middle ages." He urged that an interstate trade commission and state trade commissions be established, which shall have substantially the same power to regulate coöperation in industry, that the Interstate Commerce commissions have in regard to public utilities.

"It seems that the Interstate and State Commerce Commissions and the administrative bodies for the pure food laws point the way for the next constructive step in the development of the laws. It would perhaps be chimerical, with public opinion as at present, to propose the repeal of the Sherman law, but the situation may be met by amendments to this law. The Sherman act can be left to apply, as defined by the Supreme Court, to monopoly. Unreasonable restraint of trade may be defined as monopolistic restraint of trade, and it is rather generally agreed that monopoly should be prohibited. To make the matter perfectly clear another amendment should allow reasonable co-operation, but such coöperation should be under the watchful eyes of administrative commissions in order to protect the public.

"There can be no question that the competitive system, when unrestrained, is positively opposed to the policy of conservation. This is true alike for minerals and timber. The minerals of

¹ Abstracted by the American Mining Congress, Philadelphia, October, 22, 1913.

² President of the University of Wisconsin.

the earth require the building of the earth for their making. Mineral deposits are doubtless in the process of manufacture at the present time; but even if so, this is at so low a rate as to be negligible. From the point of view of mankind, the stores of minerals in the earth are deposits of definite magnitude upon which we may draw but once and which by no possibility can be increased. In this connection it should be recognized that modern civilization would not be possible without the mineral resources of the earth—no iron ships, no tools except those of stone, no fuel but wood. Without the sub-surface products of the earth we would at once return to the material conditions of the stone age. It is therefore incontrovertible that from the point of view of the human race, economic systems or laws which result in unnecessarily rapid use of the mineral stores of the earth are indefensible; but such are the economic theories and laws now dominant in the United States.

"The wastefulness of the competitive system may be proved with regard to every product which is taken from the earth. Lead and zinc in Wisconsin and Missouri are mined on a small scale under an extreme competitive system. The losses of these metals in their mining and metallurgy are nothing short of appalling. In southeastern Missouri, according to the late Dr. Bulkley, not less than 15 per cent of the metal is left under ground; the losses in concentration approach 15 per cent; the losses in smelting and concentration frequently amount to 15 or 20 per cent; thus making a total loss of from 45-50 per cent. These great losses are due to the system of numerous small holdings combined with the competitive system. High royalties on the part of the small feeholder are demanded of the operator. The operators desire to get large returns at the earliest practical moment upon this small investment. In consequence ore is left in the ground that should be mined; unnecessary losses take place in concentration, also unnecessary losses occur in smelting.

"But the most disastrous losses in mining as far as the future of the human race is concerned are in connection with coal. Director Holmes of the United States Bureau of Mines, in a paper upon mineral wastes, presents the facts in regard to the ruinous wastes of the unrestrained competitive system in connection with coal. He says that in the early days of mining when there was much subdivision of ownership not more than 30-40 per cent of the anthracite coal in the veins mined were brought to the surface, leaving from 60-70 per cent in the ground. He states that even at the present time not more than 50 per cent of the anthracite reaches the surface. The situation is similar for bituminous coal, but until recently the losses for such coal was substantially half. This loss has been somewhat reduced, but it continues to be appalling. Holmes estimates that since the beginning of mining in the United States, 'two billion tons of anthracite and three billion tons of bituminous coal have been left underground in such condition as to make its future recovery doubtful or impossible.' The principles which from the point of view of conservation should apply to the mining of coal are well known. So far as practicable the mines should be so worked as to make one superimposed vein after the other available. Coal slack should be reduced in amount and utilized. No considerable percentage of coal should be left in the ground as pillars. If these reforms were introduced, the losses could be reduced to half the present amounts and possibly to one-fourth.

"But to ask that any such proposals should be put into operation is purely chimerical. Under the Sherman law there is no opportunity to limit output, divide territory, or regulate prices. Five thousand bituminous operators could produce 200,000,000 tons of coal per annum beyond present demands. If the operators could agree upon limitations of output, and division of market so as to reduce freights, and could arrange for reasonable prices, which would give them no more than their present profits, they would then be able to follow these principles in mining their coal; for they themselves would be gainers in prolonging the life

of their mines, and far more important many future generations would be the immeasurable gainers in that they would have an adequate coal supply.

"Under the competitive system, we are recklessly skimming the cream of the natural resources of a virgin continent with no regard for the rights of our children or our children's children. They will have a heavy score against us if we continue to ignore the future and to apply the unrestrained competitive system in total disregard of their rights.

"My proposal to remedy these conditions is neither regulated competition, nor regulated monopoly, but retention of competition, prohibition of monopoly, permission for coöperation, and regulation of the latter. At the present time there are state and national movements to still further extend the advantages of coöperation to the farmers. Since it is unquestionable that the sense of justice of the citizens of the United States will support the courts in prohibiting class legislation, we shall, therefore, I believe, ultimately permit coöperation in all lines of business alike. If we, however, retain freedom of competition, permit concentration sufficient to give efficiency, allow reasonable coöperation, and prevent monopoly, this will require regulation just as it has been necessary to regulate the railroads. This done, the Sherman law will be forgotten. Has there been any prosecution of the railroads for violations of the Sherman law because of collusion in fixing rates? And yet, every one knows that they are just as flagrant violators of the Sherman act as any other class of corporations in the United States. Are the freight rates the same for different roads between any two points? Are the passenger rates between Philadelphia and Chicago identical on all roads? Can you do better in price by traveling over the Pennsylvania, than over any other road? The rate is the same providing the speed is the same. How does it happen that the roads all got together? Just by Providence I suppose. It was doubtless by a providential act that these rates were fixed identically upon all the roads, under the same conditions, all over the country.

"Why is it that nobody proposes to indict the railroads for collusion? Simply for the reason that the rates which they can charge are controlled by commissions, national and state. Nobody any longer wishes to make them further trouble, because the public is protected by its commissions. The railroads are just as amenable to attack under the Sherman act as any other combination in the United States, but when the railroads are giving reasonable rates, and are competing in giving reasonable service, even if the law is on the statute book and is the hallowed thing that has been described—the sense of official justice is such that they are not attacked in the courts. Will the Attorney-General of the United States or the Attorney-General of this or any other state, bring suit against the railroads for conspiracy in fixing rates when the public is properly protected? I have not heard the proposal made anywhere.

"However, it is a wrong condition when we have on the statute books a law of a kind which requires the officials of justice to close one eye whenever they pass by the men in control of one great group of industries, and at the same moment see other men not one whit more guilty. We ought to remedy this condition so that honorable business men shall not be in the position, the unfortunate position, of being technically violators of statutes which it is not advantageous from the public point of view to enforce.

"In regard to the Sherman act, it has been assumed that its only violators are the great combinations. This assumption is made in practically all discussion of the question. The Steel Trust, the Tobacco Trust, and a few other large combinations are mentioned; and it is supposed that the small business men and the small producers are not acting in violation of the law. But the principle of coöperation which the Sherman act tries to suppress extends from the great industrial centers, like Philadelphia, to the country cross-roads. Does it make any difference

here in Philadelphia, the home of anthracite, whether one buys anthracite of one retail dealer or another? It doesn't make any difference in the country cross roads either. The price is just the same from all the dealers in the same locality. The same is true of ice, the antithesis of anthracite, and is also true of all standard articles. The principle of coöperation has extended from the great manufacturers and the great dealers of the large cities to the small manufacturers and small dealers of the small cities and even villages. All are coöperating in the same way; the principle is the same for the large and small man; one is violating the law just as certainly as is the other. I am willing to stand for enforcement of law when the law is enforced alike for all; but when somebody is picked out because he is in the front seat, or because it is good politics to attack him, and ninety-nine or nine hundred and ninety-nine are allowed to escape, I say that it is a profoundly immoral situation. And that is exactly the existing situation in this country. The politician who says, 'Break up these trusts; destroy them,' says with the same breath, 'We must have coöperation among farmers.'

"Why, the cranberry growers of Cape Cod, New Jersey, and Wisconsin, sell about 90 per cent of their products through an agency down in Hudson Street, New York. Similarly many products of the farmers, illustrated by cotton, citrus fruits, etc., are marketed through coöperative selling agencies. Have we heard of the Attorney-General prosecuting these farmers? Congress understands the situation and at their two recent sessions they attached to the Sundry Civil bill a clause containing an appropriation of \$300,000 for the enforcement of the anti-trust laws, which included the provision 'that none of this money should be spent in prosecuting combinations or agreements of labor, nor spent for the prosecution of producers of farm products, and associations of farmers who coöperate and organize in an effort to and for the purpose to obtain and maintain a fair and reasonable price for their products.' The purpose of this provision is clearly to make the Sherman law class legislation by indirection and in effect to prevent equality before the law of the manufacturer as compared with the farmer. And some of the smarter state legislatures have seen the situation and in order to prevent the farmers from being hit by their anti-trust bills exempted the products of the lands so long as in the hands of the producers. You see, the state legislatures, like Congress, saw that the farmers have so many votes that they have to be dealt with gently when they form a trust. But some of the state laws got into the United States courts, and these courts promptly declared these exemptions unconstitutional as being special legislation. I venture to predict that it will not be so popular a political game to shout, 'Bust the trusts;' when the farmers understand that their trusts are also to be 'busted.' No more pernicious or immoral legislation was ever passed by Congress or by the states. The principles of justice in regard to trusts and combinations are alike for the manufacturers, the farmers and the laborers. In this country we have not a special situation which concerns a few men, but a general, irresistible impulse. There is just as close-riveted an arrangement between the three icemen in the country town as there is in steel; and any solution of the problem of combination, if it be a just solution, must be applied not only to steel, tobacco, etc., but to the small tradesman, the farmer. Just as certainly as the great combinations are violating the Sherman act, as I have no doubt many of them are, so are the small aggregations of wealth violating state anti-trust statutes. This general violation of the trust laws, national and state, is the problem that we have before us."

UNIVERSITY OF WISCONSIN, MADISON

FERTILIZER CHEMISTRY—A REPORT OF PROGRESS¹

By PAUL RUDNICK

This report is not intended to be a complete or detailed account

¹ Chairman's address delivered before the Division of Fertilizer Chemistry, September 11, 1913, at the 48th Meeting of the A. C. S., Rochester.

of the subject with which it deals; the idea has been rather to point out very briefly only the most important developments appearing in the field since the previous report under the same title presented on a similar occasion.

In addition to the process of oxidizing atmospheric nitrogen by means of the electric arc as developed by Birkeland and Eyde and by Schoenherr and the process for converting nitrogen into ammonia by the manufacture of cyanamide (Frank and Caro) and by the manufacture of aluminum nitride (Serpek),¹ we have had the announcement of the process of direct combination of nitrogen and hydrogen to ammonia by means of catalyzers in the process of Haber and Le Rossignol as described in the paper of Professor Berntsen before the Eighth International Congress of Applied Chemistry.² To the original catalyzers, iron, manganese, nickel and cobalt, have been added chromium and cerium and later osmium and uranium. The latter two are said to be superior to all the others, and with them it was possible to work at temperatures of 500° to 600° C. under high pressures at the rate of several kilograms of ammonia per hour and per liter of space occupied by the catalyzer. In the manufacturing process it has been found possible to replace osmium and uranium by cheaper catalyzers based on the improvement produced by certain additions. Electrolytic hydrogen has been replaced by hydrogen made from coal because the impurities which were poisonous to the catalyzers in hydrogen so produced were discovered and eliminated.³

It is further announced that the Ostwald process for making nitric acid from ammonia, which attracted considerable attention some ten years ago, has recently been taken up in a commercial way in England. This process is stated to depend upon the oxidation of ammonia to nitric acid by means of the catalytic action of spongy platinum or platinum black. The ammonia needed as raw material is to be obtained from the decomposition of calcium cyanamide.⁴

Recently the market has shown a considerably increased activity in calcium nitrate.

A preliminary research on the fixation of nitrogen by aluminum carbonitride has been announced.⁵

An effort to increase the price of beehive coke may furnish an artificial stimulus to the by-product coke industry and, therefore, to the production of ammonium sulfate.⁶ Increased by-product oven facilities now contemplated will, of course, add to the domestic production of sulfate of ammonia to a certain extent. The leading American by-product coke concerns report that the outlook for the industry is bright and that the market could absorb a larger production if it were available.⁷

With reference to the life of the Chilean nitrate beds it is announced that the nitrate existing in all the deposits of Chile which have been prospected, but not all surveyed, is estimated at 1,000,000,000 tons. Large supplies probably also exist on lands now but incompletely prospected. The surveyed and certified tonnage opened up at the present time ready for extracting is fully 250,000,000 tons. The probable life of the surveyed deposits is at least several hundred years, even allowing for a steadily increasing annual rate of consumption.⁸ An excellent description of the Chilean nitrate fields by Dr. W. S. Tower has just appeared.⁹

In connection with the many processes proposed for the production of available phosphoric acid from phosphate rock by means other than acidulation with sulfuric acid, it is claimed that a product analyzing 45 per cent of available phosphoric

¹ THIS JOURNAL, 5, 335.

² *Ibid.*, 4, 760.

³ *Chem. Ztg.*, 37, 584.

⁴ *Mel. Chem. Eng.*, 11, 438.

⁵ *Am. Feriz.*, 39, 25.

⁶ *Mel. Chem. Eng.*, 11, 427.

⁷ *Am. Feriz.*, 39, 37.

⁸ *Ibid.*, 39, 56d.

⁹ *Pop. Sci. Mon.*, 83, 209.

acid, 12 per cent ammonia, and 5 to 6 per cent of potash is now being produced commercially.¹ The explanation of the process given is that instead of sulfuric acid a plant food is used in the new process. From another source² we learn that in this method the phosphate rock is treated in an electric furnace, the phosphoric acid being recovered in vapor form. It is stated that the new method cannot be worked successfully with a higher current cost than \$4 per horse power per annum, which is a much lower figure than has ever been attained in this country.

In this connection it must be considered that the utilization of sulfur-bearing gases is undoubtedly increasing right along, chiefly because of the damage which, it is claimed, is being done by these gases. The electrolytic precipitation process of Cottrell³ and the thiofen process, in which the sulfur is recovered as elementary sulfur, seem to be making satisfactory progress.⁴

An extended review of possible sources of potash in the United States by Cameron has appeared recently.⁵ It covers in addition to the minor sources the more important possibilities such as alunite, salines and salt beds, feldspar, green sand marls and kelp. The possibility of recovering potash from the flue dust of cement plants in which potash feldspar is used instead of clay or shale is also described. The manufacture of potash from kelp has apparently reached the commercial stage, judging from a recent advertisement.⁶

The extraction and refining of oil and of the production of ammoniates from the Pacific Coast Fisheries is apparently attracting attention in a commercial way and this may present some interesting chemical problems to the fertilizer chemist for solution.

The controversy between various authorities on the theory of soil fertility, including a satisfactory theory of fertilizer action, is still active, but no important new developments have been recently announced.

ARMOUR AND COMPANY
UNION STOCK YARDS, CHICAGO

FOOD STANDARDS AND THEIR EFFECT UPON FOOD LAW ENFORCEMENT⁷

By FLOYD W. ROBISON

From a standpoint of food law enforcement, there has been quite a constant official pressure toward the creation of food standards. Food standards have had much to do with improving the quality of foods, and it is therefore with full appreciation of this condition that we venture for purposes of discussion a few points bearing on the effect of standards as written in the law on food law enforcement.

Obviously, the analyst when passing upon the purity of a food product must have some standard in mind. It is either an expressed standard or an understood standard. Such a standard, if followed, should be one that will allow the widest liberty to the pure product. Primarily it should be borne in mind that a food product cannot in justice be suited to the limitations of the analyst. With manufactured foods the widest latitude must likewise be given for individuality of manufacture and room should always be allowed for a variation in standard due to actual improvement in process of manufacture.

It has been the aim of many food law officials to incorporate in the laws of the various states as many food standards as possible. In so doing the work of the food analyst and the food department has been very materially simplified. In plain words, a violation of the law may in this way be more clearly and more surely perhaps pointed out to a jury of twelve men. This

at first glance may seem very desirable but it is the actual working out of the plan that we should observe. Let us take a specific case, for example, cider vinegar.

Until the present year the Michigan statute required that a fermented vinegar should have not less than 4 per cent of acetic acid, $1\frac{3}{4}$ per cent solids and $\frac{1}{4}$ per cent ash. It becomes perfectly simple then to sustain a case in court where the solids are $1\frac{1}{2}$ per cent or where the ash may be $\frac{1}{5}$ per cent without taking into consideration at all the question of the real purity of the product.

On the other hand, it becomes extremely difficult to prove an infraction of the law when the standards set in the law are met by the food product in question. We have had states' attorneys actually refuse to enter complaint in the case of a totally sophisticated product, because so far as its standard was concerned it complied with the figures set in the law.

Food standards in so far as they effect other than the essential constituents of that product when placed in the statute become actually a standard of adulteration instead of a measure of purity.

Another point: improvement of product should always be encouraged by a food law. Many times a set standard in the law works actual hardship upon a manufacturer, who by expensive and painstaking devices and processes has improved his product, and incidentally in so doing disarranged perhaps its several unessential constituents.

Referring again to cider vinegar, we hold that pure cider vinegar should have not less than 4 to $4\frac{1}{2}$ per cent of acetic acid, derived from cider. Now the essential requirements concerning cider vinegar are first, that it must be manufactured from cider, and second, that it must have not less than a certain amount of acetic acid. Suppose it becomes desirable in the process of manufacture to clarify a product by any of the methods in use or by other desirable methods not now current. Provided the acid is not disturbed nor the cider value impaired, it is manifestly fair that such improvements should be permitted, yes, encouraged by the law.

In coffee, tea, spices, in fact in nearly all products the inclusion of a standard in the law, other than as indicated above, becomes a source of embarrassment at times to the conscientious official, and at the same time a menace to the business of the wide-awake, progressive manufacturer.

It is convenient for a food official to be able to say to the manufacturer: "Why the law states that your product shall contain a certain ratio of its constituents and it becomes my duty to enforce this law." As we have stated heretofore, this simplifies the duties of the food official. The ratio has been read into the law, not because it bears any relation to the food value or to the food purity, but because perhaps many analyses of the product now on the market or produced heretofore show a certain ratio of these constituents. Actual progress under these conditions is impossible.

Vanilla extract is another example. We are firm in our opinion to date that the very best Vanilla Extract that has been produced has been produced by a method quite similar if not identical with the U. S. P. method, yet it would be absurd to prescribe in the law that besides a certain vanillin content, the extract must contain a certain quantity of resins and other non-valuable constituents of the vanilla bean.

It is not essential, neither is it desirable that a law guarding the purity of maple syrup should state the content of ash, or any standard other than that of sugar content accompanied by the injunction of absolute purity. It is a fact that many farmers priding themselves on the purity and excellence of their maple syrup do actually add clarifying ingredients, etc., for the very purpose of securing greater purity and thereby a more salable product. Such efforts should be encouraged and a law should not prohibit progress of this kind.

¹ *Manuf. Rec.*, July 21, 1913.

² *Am. Ferts.*, 39, 38.

³ *This Journal*, 3, 542.

⁴ *Am. Ferts.*, 39, 55; also *This Journal*, 5, 955.

⁵ *Com. Ferts.*, 7, 22.

⁶ *Am. Ferts.*, 39, 20-21.

⁷ Presented at the 48th Meeting of the A. C. S., Rochester, September 8-14, 1913.

The standard is most properly the analysts' guide and should be promulgated for that purpose. To incorporate a standard in the law other than to regulate as we have stated above the minimum strength of the essential ingredient or the maximum amount allowable of any specially undesirable constituent is to place a premium upon analytical incompetency.

There are places where the standards can be stated and may be properly incorporated in the law. This includes the fat and solids in milk, but not the ash nor the specific gravity nor the refractive index of the serum. Likewise the acid of vinegar but not the solid, ash, alkalinity, glycerine, nor the other non-valuable constituents. The vanillin content of vanilla extract per-

haps; the citral content of lemon extract; the arsenic and lead limits in foods and food colors; and the maximum amounts of preservatives, if permitted, may be made a part of the law with perfect propriety.

The standard laid down in the law should be the minimum quantity permissible of the desired constituent or the maximum quantity allowable of any undesirable ingredient, and for purposes of food law enforcement, it will be found, we think, preferable to limit the standards, in so far as they are read into the law, to practically these two conditions.

DETROIT TESTING LABORATORY
DETROIT, MICHIGAN

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

AN AUTOMATIC CHEMICAL FEEDER

According to *Engineering Record*, 68, No. 10, 264, an automatic type of chemical feeder has recently been tested at the hydraulic laboratory of the University of Illinois by the patentee, Ralph Hilscher. The apparatus works in conjunction with a Venturi meter and depends for its action directly on the decreased static head at the restricted section.

Referring to the sketch, the device consists of a box divided into two compartments by a wall which extends from the bottom to within a short distance of the top. At the top of this wall is pivoted a horizontal arm, from which are suspended two floats of equal dimensions, one in each compartment, and at equal distances from the pivot. The arm in compartment B extends beyond the float and connects with a balanced valve on the end of a feed pipe, which supplies chemical from a supply tank. The valve is so made that when the float in B falls below the

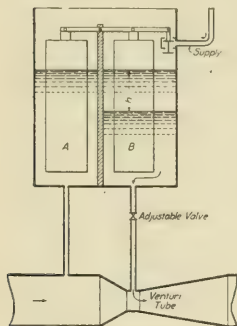


Diagram of Chemical Feeder

float in A the downward movement of the arm will cause the valve to open and admit chemical solution to compartment B.

Connecting compartment B with the reduced section of a Venturi tube is a pipe in which there is an adjustable valve. Another pipe connects A with the full section of the Venturi tube. The Venturi tube is inserted in the pipe to which it is desired to feed the chemical.

When a flow of water occurs through the Venturi tube unequal pressures at the full and reduced sections will tend to make the levels in A and B different, that in B being lower. This difference in pressure, represented by h , is proportional to the square of the rate of flow through the Venturi tube and, if utilized to force chemical solution through an orifice, will produce a flow through that orifice directly proportional to the flow in the main. The adjustable valve acts as an orifice in this device and the desired effective head on it is established by building up the level in B equal to that in A. As already explained, these two levels are kept the same by the float arrangement.

Referring to the test sheet, the figures are for four different tests, each with a different size of opening of the adjustable valve. The first column contains the quantities of water treated, measured in a large tank at the end of each run. Column 2 contains the corresponding quantities of solution fed by the machine, determined by measuring the drop in the supply tank. Column 3 gives ratios of Column 2 to 1, and these figures should all be the same theoretically for a given size of orifice. The ratios are averaged for each test, and in the sixth column are

TESTS OF AUTOMATIC CHEMICAL FEEDER

Gallons treated	Gallons solution applied	Ratio of Col. 2 to 1	Time of run, in minutes and seconds	Gallons per minute treated	Per cent by which ratio departs from average
639	2.98	214	5.39	113	+6.2
726	3.49	208	6.30	112	+3.2
682	3.58	190	5.12	131	-5.8
1495	8.03	186	10.11	146	-7.7
1382	6.59	210	17.10	80	+4.3
Average.....		202			
1620	5.85	277	9.20	174	+1.8
1014	3.80	267	18.55	54	-1.8
Average.....		272			
1294	2.98	434	19.30	66	-0.2
1680	3.94	426	10.00	168	-2.1
1355	3.04	445	14.30	93	+2.3
Average.....		435			
1365	3.55	384	13.30	101	-4.8
1506	3.58	420	26.00	58	+4.0
1653	4.07	407	10.00	165	+0.8
Average.....		404			

given the per cents by which the various ratios depart from the average. By reference to the fifth column it will be seen that rates at which water was treated varied by about 300 per cent.

MICARTA AND BAKELITE MICARTA

Micarta is a new material which has been developed by the Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pa., to take the place of hard fiber, glass, porcelain, hard rubber, built-up mica, pressboard, rawhide, moulded compounds, etc.; it is used for commutator bushings, brush-holder insulation, as noiseless gear blanks, as conduit for automobile wiring, as spools for spark coil and magnet windings, for refillable fuse tubes, for wireless coil separators, for arc shields in circuit breakers, for water-meter discs, etc.

Micarta is a tan-brown colored, hard, homogeneous material having a mechanical strength about 50 per cent greater than hard fiber. It can readily be sawed, milled, turned, tapped, threaded, etc., if a sharp pointed tool is used, and the work done on a lathe. It can be punched only in thin sheets and cannot be moulded. Micarta is not brittle, and will not warp, expand, nor shrink with age or exposure to the weather, but takes a high polish, presenting a finished appearance.

Two grades of the material are made. The grade known as bakelite micarta will stand a temperature of 150° C. continuously, or 260° C. for a short time. It is infusible and will remain unaffected by heat until a temperature sufficient to carbonize

it is reached. Heat will not warp bakelite micarta, and it will stand an electric arc better than hard fiber, hard rubber, built-up mica, or any moulded insulation containing fibrous or resinous materials. Its coefficient of expansion is low, being approximately 0.00002 per degree Centigrade.

Bakelite micarta is insoluble in practically all of the ordinary solvents, such as alcohol, benzine, turpentine, and weak solutions of acids and alkalis, hot water and oils. It is indifferent to ozone—an advantage over hard rubber, resins, etc., for electrical purposes. It is non-hygroscopic and impervious to moisture.

The other grade designated as No. 53 micarta has the same mechanical and electrical properties as the bakelite micarta, but differs in its chemical and thermal properties. The plain micarta behaves toward chemicals and heat very much as an ordinary resin. This grade is not used in plate form.

NEW CENTRIFUGAL PUMP

The *Engineering Record*, Oct. 4, 1913, reports that a new centrifugal pump ranging in size from 2 to 15 inches and suitable for low speeds is being placed on the market by a Philadelphia company. The casing is made solid with a detachable suction head and carries on the top a detachable flange which supports the stuffing box and thrust bearing. By removing the bolts in the upper flange the casing may be opened for inspection of the impeller without disturbing the suction or discharge flanges. The casing is of cast iron and is fitted with removable bronze bushings. The thrust bearing, which is of the radial ball type, is carried on the pump housing and is fitted with a sight feed lubricator. The guide bearings are lubricated automatically. The impeller is of the closed type. The frame is of channel iron with suitable braces which carry the guide bearings, and the motor is supported on a cast-iron base.

TESTING THE LIQUOR IN SULFITE COOKS

Paper 13, No. 4 (Oct. 8, 1913), reports that according to *Papierfabrikant* the digesting liquor is not fully utilized in the manufacture of sulfite cellulose because the samples are improperly obtained. Generally the digesting liquor is run off into a copper beaker or a glass vessel, cooled slightly or not at all and then titrated. The SO_2 when heated or agitated is changed from the liquid into the gaseous form, and as the specimen of liquor is agitated and heated very greatly when drawn off, a large part of the SO_2 escapes. If a digester whose total content of SO_2 amounts to $3\frac{1}{2}$ to 4 per cent is heated up to 100°C . with gas escaping, scarcely more than 2 per cent SO_2 will be found.

Therefore, if it is desired to determine the correct proportion of SO_2 in the liquor, it is recommended to attach to the delivery outlet pipe a rubber tube or a leaden worm of thin piping, the end of which is provided with a cock, and place the worm in cold water. The liquor should then be run off cold and titrated, when it will be surprising to find how strong it still is.

THE PRESENT STATUS OF THE GLASS BOTTLE AND HOLLOW WARE INDUSTRIES IN THE UNITED STATES¹

Although the first automatic bottle machine was introduced in 1904, until 1912 its advance was rather slow, owing to the fact that the shops of the Owens Bottle Machine Company were limited to an output of 50 machines per year. In January, 1913, however, this company completed a new plant and it now has a capacity of 100 new-style 10-arm machines a year. These machines, which are said to be complete in general principle, have almost twice the output of the old 6-arm machines, the

production being 400 gross per day of $\frac{1}{2}$ -ounce to 6-ounce bottles, 200 gross of 6-ounce to 32-ounce size, and 100 gross of gallon size. The installations and machines on the order of the Owens type in the United States in 1912, as compared with 1911, were as follows:

	1911	1912
Total installed.....	103	133
Total ordered.....	18	33
Total (a).....	121	166

(a) Aggregate annual capacity, 7,000,000 gross of bottles.

The development of automatic lehrs has kept pace with the machines, in order to handle the increased production.

According to Wheeler (*Intern. Soc. Rev.*, November, 1912), it is not likely that the Owens Company will turn out more than 100 more of the 10-arm machines for several years, as the number of machines made and in use by 1914 will be able to supply almost the entire demand for bottles in the United States, Canada and Mexico. The annual consumption will hardly reach 15,450,000 gross in 1914, unless a greater demand can be induced by a greatly lowered price. It is predicted that in two years the bottle industry will belong to the automatic machine, although there are certain classes of ware which may never be taken over by the machine; and it is estimated that by 1914 there will be 250 automatics in operation. At present, the machine is manufacturing almost every type of bottle from $\frac{1}{2}$ -ounce size to 12-gallon demijohns, and a number of large companies, including firms controlled wholly or in part by the Owens Company, are in a most commanding position in the bottle market. In fact, these concerns are preparing to take over the entire bottle industry. The Fairmont, W. Va., plant of the Owens Bottle Machine Company is the best automatically equipped bottle factory in the world; the production amounts to about 500,000 gross of bottles of all kinds per year.

Among the other types of machines, the Whitall-Tatum automatic machine is said to be capable of competing with the Owens machine.

Notwithstanding the rapid changes constantly going on in bottle-making machinery, at present there is an increase in the number of semi-automatic wide-mouth machines installed. In 1912, 33 plants were equipped with 170 machines of this type; to-day there are 37 factories operating 201 machines. With regard to narrow-mouth machines, it may be noted that 96 United and O'Neill machines, employing 487 journeymen, were in operation in August, 1913. The United machine (semi-automatic) is capable of producing $85\frac{1}{3}$ dozen of bottles per man a day.

Owing to the number of blownware furnaces which were constructed and started during the blast of 1912-13, the prospects for the manual blower are somewhat brighter than at any time during the past six years. This is mainly attributed to bringing the cost of production of the blownware bottle closer to that made by the automatic machines. In June, 1913, 609 workmen were reported idle by the Glass Bottle Blowers' Association—801 less than in June, 1912.

As to the visible stocks of blownware on hand at various factories in August, 1913, only 17 per cent of the plants reported heavy stocks. In certain instances, heavy stocks of automatic ware were reported, states *The Glassworker*, August 9, 1913, 12, although the opinion is authoritatively expressed (*National Glass Budget*, 28, No. 28, 1) that the Owens Company's product is maintaining its pre-eminence in the trade, owing to quality, accurate and uniform weight and capacity, and low cost of manufacture (high productive capacity of the machines and low cost of labor involved).

A list of the manufacturers of glass bottles and hollow ware in the United States follows. The value of the glass bottles and hollow ware produced annually in this country is now approximately \$50,000,000.

¹ For a review of the status of the window glass industry in the United States, see *THIS JOURNAL*, 5, 80; and for a discussion of the conditions prevailing in the plate glass industry, see *THIS JOURNAL*, 5, 253.

A LIST OF THE MANUFACTURERS OF GLASS BOTTLES AND HOLLOW WARE IN THE UNITED STATES

Including manufacturers of prescription bottles and vials; medicine reagent and liquor bottles; packers' and preserved bottles, beer and mineral water bottles, milk bottles, and fruit jars.			Products		
Plants and location	Method	Continuous tanks	Rings	Furnaces	Pots
A., automatic; H., hand; M., machine(s)					
B., bottle; G., glass					
California					
Illinois-Pacific G. Co., San Francisco	M. and H.	4	37	...	General line
Pacific Coast G. Works, San Francisco	M. and H.	2	16	...	General line
Georgia					
Tallapoosa G. Mfg. Co., Tallapoosa	A., automatic; H., hand, M., machine(s)	1	Prescription, medicine, mineral water, and liquor B., V. and F.
Illinois					
The American B. Co., First National Bank Bldg., Chicago	A. M. and H.	42	Beer and mineral water B.
Chicago Heights G. Co., Chicago Heights	M. and H.	2	24	...	General line
The Headley G. Co., Danville	M. and H.	1	12	...	Prescription, mineral water and beer B. V.
Illinois G. Co., Alton	A. M. and H.	10	General line
Ohio Beer & Glass Co., E. St. Louis	M. and H.	3	26	1	General line
Ohio B. Co., Olney	M. and H.	1	10	1	Liquor B. and F.
Schram Automatic Sealer Co., Hillsboro	8 semi-A. M. and H.	1	8	...	Packers' and preservers' B.
Wilcox G. Co., Inc., Robinson	M. and H.	1	6	...	Prescription and liquor B. and F.
Indiana					
Bell Bros. G. Mfg. Co., Muncie	A. M.	14	159	...	Packers' and preservers' B. and jars
Bell B. Co., Fairmount	M. and H.	1	16	...	Liquor B. and F.
Daleville G. Co., Daleville	M. and H.; 22 shops	General line
Fairmount G. Works, Indianapolis	M. and H.	2	28	...	General line
Globe G. Co., Arcadia	M. and H.	1	10	...	Medicine and liquor B., F. and V.
Graham G. Co., Dept., Majestic Bldg., Indianapolis	17 M.	3	Beer and water B.
Okefenokee Glass Co., Okefenokee	M. and H.	1	24	...	Liquor B. and F.
Lapel B. Co., Lapel	M. and H.	2	6	...	General line
Marion Flint G. Co., Marion	M. and H.	2	24	...	General line
Maring Hart & Co., Dunkirk	M. and H.	2	22	...	General line
Model G. Works, Ellettsville	M. and H.	2	14	...	Beer and water B.
Norfolk Glass Co., Norfolk	O'Neill M. and H.	3	...	102	General line
Pennsylvania G. Co., Anderson	M. and H.	2	13	...	General line
Root G. Co., Terre Haute	M. and H.	3	26	...	Beer and water B.
Sims G. Works, Sims	M. and H.	1	8	...	General line
Skilleen-Goodin G. Co., Yorktown	M. and H.	2	14	...	Packers', preservers', and milk B.; fruit jars
Sneath G. Co., Hartford City	M. and H.	1	1	16	General line
Standard G. Co., Ellettsville	M. and H.	1	8	...	Medicine and V.
Turner Bros. G. Co., City	5 A. M. and H.	3	36	...	General line
Upland Flint B. Co., Upland	M. and H.	2	20	...	General line
Western Flint B. Co., Eaton	M. and H.	1	10	...	Medicine and liquor B.
Woodbury G. Co., Winchester	M. and H.	2	12	...	Liquor B. and F.
Woodbury G. Co., Winchester	M. and H.	3	36	...	General line
Kansas					
A. H. Kerr & Co., Altoona	M.	1	10	...	Fruit jars
Maryland					
The Buck G. Co., Baltimore	M. and H.	1	7	...	General line
Carr-Lowrey G. Co., Baltimore	M. and H.	1	...	33	Paste mold ware, stoppers, and a general line of B. and jars
Maryland G. Corporation, Baltimore	M.	3	11	...	General line
Swindell Bros., Baltimore	M. and H.	1	...	38	General line
Michigan					
Michigan G. Co., Saginaw	M. and H.	1	6	...	General line
Monroe G. Co., Monroe	Semi-A. M. and H.	1	8	...	Packers', preservers', and ointment B. and jars
Missouri					
Adolphus Busch G. Mfg. Co., St. Louis	1	1	25	...	Beer B.
New Jersey					
Cape May G. Co., Cape May Court House	M. and H.	2	21	...	Prescription, beer, and water B.; V. and F.
Combs G. Co., Trenton	M. and H.	1	8	...	General line
Cumford G. Mfg. Co., Bridgeton	M. and H.	6	69	...	General line; also battery and ointment jars
Gayner G. Works, Salem	M. and H.	2	Battery jars, carboys, water B.; general line of large ware
Hersford G. Co., Cape May Court House	M. and H.	1	9	...	Prescription, beer and water B.; V. and F.
More-Jonas G. Co., Cape May G. Co.	M. and H.	4	28	...	General line
Parke Bros. G. Co., Bridgeton	M. and H.	1	14	...	Medicine and packers' and preservers' B.
Farmer & Co., Clayton	M. and H.	1	...	5	Medicine, beer and water B.; V.
Salem G. Works, Salem	M. and H.	...	23	16	General line
South Jersey G. Works, Swedesboro	M.	2 of 20 tons each	Beer and mineral water B.
Star G. Co., Medford	M.	1	10	...	Druggists' supplies, liquor B. and F.

[illegible]

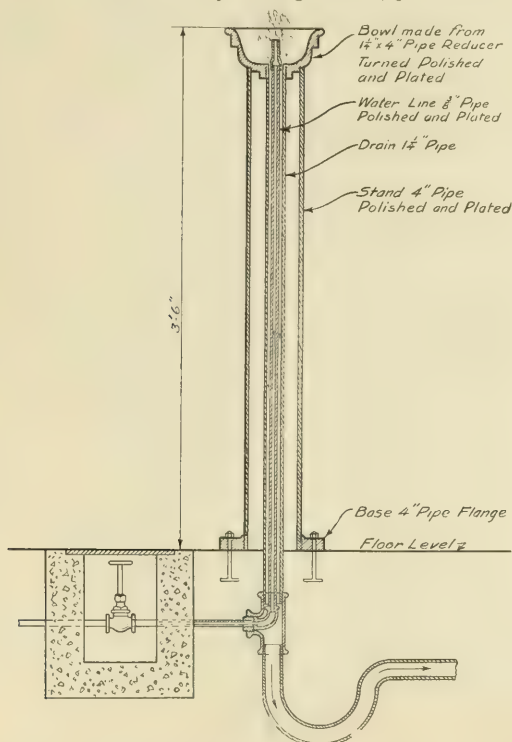
A LIST OF THE MANUFACTURERS OF GLASS BOTTLES AND HOLLOW WARE IN THE UNITED STATES—(Continued)

Plants and location	Method		Rings per doz.	Pats.	Products
	A. automatic, M. machines	H. hand, Continuous tanks			
Spring City G. Works, Ltd., Spring City					B., bottle(s), F., flask(s); V., vial(s)
Thatcher Mfg. Co., Kane, Pa.; Strasburg, Ill., Pomeroy, N. Y.					Prescription, beer and water B., and F.
Tibbs Bros. G. Co., Sharpsburg	Owens A. M.	6		30	Fruit jars and milk B.
Wrightman G. Co., Parkers Landing		1	8		General line
Wilcox G. B. Co., Wilcox		1	8		Prescription B. and V.
Wormser G. Co., Pittsburgh		1	12		Prescription, beer, water, and liquor B., and F.
South Carolina					
Carolina G. Co., Columbia		1	9		General line of B. and jars
Laurens G. Works, Laurens		1	6		Prescription and beer B., and F.
Tennessee					
Chattanooga B. & G. Mfg. Co., Alton Park	M. and H.	3	17		General line
Texas					
Fort Worth G. Mfg. Co., Fort Worth		1	6		F.
Virginia					
Alexandria G. Works, Inc., Alexandria		1	9		General line
American G. Works, Inc., Richmond		1	10		General line of B.
Belle Pre B. Co., Alexandria	M.	1	8		Milk B.
Central States G. Co., Bridgeport		2	10		Prescription and liquor B., and F.
Old Dominion G. Co., Alexandria	M. and H.	2	12		General line of B.
Piedmont G. Co., Salem		1	6		Prescription B., fruit jars, F.
Virginia G. Co., Alexandria		1	8		Packers', preservers' and beer B., and F.
Washington					
Anacortes G. Co., Anacortes		1	4		Packers' and preservers' jars and B.
West Virginia					
Duquesne G. Co., Paden City		2	8		Beer and water B., etc.
Fairmont B. Co., Fairmont	M. and H.	1	8		General line of B.
Hazel Atlas G. Co. (General offices, Wheeling); factories at Washington, Pa., and Clarksburg, W. Va.					
Kanawha G. Co., Cedar Grove	M. and H.	16			Milk, packers' and preservers' B.; fruit jars
North Wheeling G. Co., Wheeling	M. and H.	1	10		General line of B.
Owens Eastern B. Co., Clarksburg	M. and H.	2	12		General line of flint and amber B.
The Standard Milk B. Co., Parkersburg	6 Owens A. M.			3	Medicine B. and pharmaceutical ware
Travis G. Co., Clarksburg	Warner M.	1	8		Milk B.
Tygart Valley G. Co., Grafton	A. M.	2	20		Milk B. and jars
	M.	1	8		Packers' and preservers' ware, and fruit jars
Wisconsin					
Wm. Franzen and Son, Milwaukee	United M.	3	32		Beer and mineral water B.

[NOTE—We are indebted to Mr. George B. Kimes, of Pittsburgh, Pa., who courteously furnished much valuable information.—W. A. H.]

A SANITARY DRINKING FOUNTAIN

The details of a sanitary drinking fountain, 52 of which are



in use at the Gary plant of the American Sheet and Tin Plate Company, are shown herewith.

THE SCORIA BRIQUETTING PROCESS

Methods that have been developed for efficient means of turning the wasteful expense of handling and recharging flue dust into a productive factory are fairly numerous. According to Ernest Stütz in the *American Institute of Mining Engineers*, the Scoria briquetting process has been in such successful operation for over two years on a daily capacity of 200 tons at the Rheinhausen works of the Friedrich Krupp A. G., that the installation has recently been doubled.

In this method a binder is used, but with the distinction that, between manufacture and use, the material so employed undergoes an essential transformation, being hydraulic until it passes into the furnace, and being there turned automatically into a fusion binder. The metallic oxides are thus free to react during their passage through the region of the top gases, and the binder gives the briquettes the necessary consistency to support the weight of the stock pile.

One briquetting press turns out from 1,800 to 2,000 briquettes per hour. Taking the weight per briquette at 8.8 pounds, this gives 144 to 160 tons per 20-hour working day, about 45,000 tons of briquettes per year.

In this process, granulated slag and lime are mixed with the valuable materials and made hydraulic in rotating drums where they are exposed to moderate-tension steam. When thoroughly mixed, sifted, and ground, the powdery mass is pressed into bricks, which are carried in train-loads of trolleys to cylindrical kilns, in which they are hardened by being exposed to the action of high-tension steam for from 8 to 10 hours. The train-load of hardened bricks goes straight from the kiln to the blast furnace and is there dumped, unless required for immediate use.

The manufacture is almost automatic. If the necessary amount of steam is provided for, there is nothing in the process itself that requires supervision. The transportation is practically all mechanical, the briquettes being handled only in transferring them from the press to the trolleys before hardening. The labor required for an installation of two presses consists of a foreman and fourteen men, including labor for steaming drums, grinding and conveying machinery, presses, hardening kilns,

and trolley transportation. The plant operation requires nothing in the way of special experience, skill or supervision. Raw materials are always at hand and the success of briquetting is independent of special conditions of the flue dust.

In the Scoria process no air drying is necessary and this distinguishes it from all other briquetting processes. Savings in space and handling are also considerable factors in its economical advantages.

The hydraulic binder gives the body the necessary consistency at a minimum consumption of binding material, and, being in the nature of a hydrosilicate, leaves the oxides freely accessible to the top gases. It is not necessary in the case of the Scoria binder to have enormous pressure on one side of the briquette to produce an actual flow of gas through the structure. Also the temperature necessary for the destruction of the hydrosilicates is above that where sintering commences, so that there is no possibility of the briquettes crumbling away prematurely.

In practice, a very important coke economy will result from the use of the Scoria process. Working with a homogeneous and naturally piled stock column, gases can circulate and pass up under equal pressure, while combustion will be far more complete and the production of carbon monoxide will be lessened; it has been proved by actual operation in Germany that a saving of from 15 to 20 per cent of coke has been effected. The inventor of the process feels confident that it is quite possible to perfect operating conditions so as to produce one ton of iron per day for every cubic meter of blast-furnace volume.

The Scoria plant may be used to produce excellent slag building brick, and could alternate their manufacture with the production of flue-dust or fine ore briquettes at a moment's notice, the operations being almost identically the same, except that the flue dust or fine ore is left out of the mixture. Such bricks have shown ample strength for all purposes, not only under severe laboratory tests, but also in actual use for building purposes during a number of years.

Cost of production (not counting the slag as having a value) in Germany, on a two-press installation capable of furnishing 24,000,000 brick per year, is about \$1.25 per thousand.

EXPOSURE TESTS OF COPPER, COMMERCIAL ALUMINIUM AND DURALUMIN

A paper on the above subject, read by Prof. E. Wilson, before the British Association at Birmingham, described a continuation of tests upon the influence of exposure in London on the electrical conductivity of light aluminum alloys, reports of which have been made from time to time. Each specimen is in the form of wire 0.126 in diam. and 70 feet long. After two years' exposure, the percentages increase of electrical resistance taken on the values in 1911 at 15° C. are as follows:

High conductivity copper.....	2.0
Commercial aluminum.....	4.4
Duralumin.....	8.2

Duralumin is a copper-manganese-magnesium alloy of high tensile strength and exposure has apparently made it more brittle.

ELECTROLYTIC COATING OF IRON AND STEEL WITH LEAD

According to *The Electrician* for September 26, 1913, an English company has acquired a process devised by Mr. Sherard Cowper-Coles for coating iron and steel with lead electrolytically. It is stated that lead can thus be economically deposited up to a thickness of one-eighth inch, and that the method is suitable for protecting iron and steel from corrosion, and for the lining of pipes, tubes and chemical vessels for containing corrosive liquors. Steel plates coated by this process are much smoother than the ordinaryterne plate and there is no reduction in tensile strength or ductility. The process can also be used for the

coating of earthenware and wood and for the protection of ornamental iron work. The cost is stated to be low.

TANNIC ACID FROM SPENT SULFITE LIQUOR

According to *Tidskrift for Papirindustri* as reported in *Paper* 13, No. 4, 23 (Oct. 8, 1913), Hans Lundmark, Drammen, Norway, has succeeded in reclaiming tannic acid suitable for tanning leather, from waste sulfite liquors. The acid ought, however, to be used only in admixture with some other material, as it is said the tanning process then takes less time. The tannic acid from waste sulfite liquor is said to be very cheap. Some important tanneries in England are now trying out this acid.

Mitscherlich and other chemists have, as is generally known, experimented considerably with the preparation of tanning material from the above source, but with indifferent success.

A NEW DESULFURIZING METHOD

The *Engineering and Mining Journal*, July 5, 1913, describes the Hall process of desulfurizing sulfide ores with eradication of noxious smelter fumes as entirely novel, being based upon the principle of removing the "fixed" sulfur atom of a sulfide by distillation, without permitting any considerable portion of the sulfur thus discharged to pass into any combined forms, such as SO₂ or SO₃.

The distillation of both fixed and free sulfur as such constitutes the advantage this method has over the other sulfur-recovery processes. Eliminating the sulfur as oxide with subsequent reduction means that a large amount of free oxygen must be taken care of before the sulfur reduction begins, thus requiring extra expense for reducing agents, while the fuel expense of removing oxygen combined with sulfur from such association is greater than the fuel expense of direct distillation.

Tests have been made to determine how complete a desulfurizing could be produced in this process; many analyses show less than 1 per cent of total sulfur remaining in the cinder. The distillation is obtained by the direct application to the ore of a burning gas flame of slightly reducing or, at least, non-oxidizing character, accompanied by H₂O, either in the shape of water of formation (from the combustion of hydrogen) or of extraneous water in the shape of steam which is decomposed by the hot ore. The nascent oxygen goes to the metal and the nascent hydrogen combines with any free oxygen that may enter the furnace by means of the atomizer through which the gases are admitted, thus creating a sort of cycle of H₂O decomposition and water formation from the combustion of the hydrogen so derived.

When the furnace burners are properly adjusted, the final discharge of hydrogen appears to be all in the shape of water vapor, *i. e.*, complete balances are easily maintained so that there is substantially neither SO₂, SO₃, COS nor H₂S in the discharge, tests being made on samples taken within a distance of six inches from the furnace.

A large variety of ores have been worked, including pyrites, various pyrrhotites, copper concentrates, crude blende and zinc concentrates. The action appears to be the same on each. In order to prove that the "fixed" atom is removed by distillation, the furnace has been operated on chemically pure FeS; no SO₂ or H₂S was discernible in the discharge, but only yellow elemental sulfur vapor.

The analyses of the cinder show it to be a mixture of Fe₂O₃ and Fe₃O₄. The temperature maintained in the furnace must be slightly above 700° C., as that is about the distilling point of the sulfur of a metallic sulfide, and it must be maintained below 900° C., the fusing point—a large margin of safety.

Although undoubtedly the reaction is somewhat exothermic, no allowance has been made for this in the fuel calculations, fuel required being calculated as if the reaction were entirely endothermic; on such a basis, allowing amply for radiation

and for the largest factors of safety, numerous engineers have calculated the amount of coal fuel required (gasified) at less than 10 per cent of the weight of the ore.

The cost of producing sulfur by this method in American smelting works is placed at from \$3 to \$5 per ton of the crude sulfur derived.

The fumes coming from the smelter are of a heavy yellow appearance with the odor of hot elemental sulfur vapor. The sulfur is extracted from the fumes by simple washing, as it is found that it has great physical affinity for water, due, presumably, to surface tension, when the fumes are agitated with

water, the atmosphere is almost instantly clarified, the sulfur settling to the bottom of the apparatus.

This sulfur has been analyzed several times and found to be from 98 to 99 $\frac{1}{2}$ per cent pure, the impurities being flue dust or lead or zinc sulfides. The refined sulfur has been found to be over 99 $\frac{1}{2}$ per cent soluble in CS₂, and is of the octahedral and prismatic types. The fumes have also been run through the Cottrell electrical dust collector, which completely precipitates the sulfur.

The process has been developed principally with a view to attaching it to multiple-hearth roasters, but promising experiments have been made towards its adaptation to blast furnaces.

SCIENTIFIC SOCIETIES

AMERICAN CHEMICAL SOCIETY—FORTY-EIGHTH MEETING, ROCHESTER, SEPTEMBER 8-12, 1913

DIVISION REPORTS

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

After the transaction of the usual routine business and the reading of the papers as presented in the program given in *THIS JOURNAL*, 5, 868, the following officials were unanimously elected for the ensuing year:

Chairman, Floyd W. Robison; *Vice-Chairman*, R. A. Harcourt; *Secretary*, Glen F. Mason; *Executive Committee*, A. V. H. Mory, L. M. Tolman, H. A. Huston.

G. F. MASON, *Secretary*

FERTILIZER CHEMISTRY DIVISION

The meeting was called to order by Mr. Paul Rudnick, Chairman. After the transaction of the usual routine business, the program was rendered as printed in *THIS JOURNAL*, 5, 868.

The Executive Committee was authorized to prepare a plan for the future handling of the analytical and research work of the division.

The following officers were elected for the ensuing year:

Chairman, J. E. Breckenridge; *Vice-Chairman*, E. L. Baker; *Secretary*, F. B. Carpenter; *Executive Committee*, Paul Rudnick, F. K. Cameron, C. H. Jones, H. J. Wheeler.

J. E. BRECKENRIDGE, *Secretary*

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

This Division met at Rochester University, with Mr. William Brady presiding.

After the transaction of the usual routine business, the financial condition of the division was reported as follows:

Money received.....	\$234.62
Disbursements.....	39.00
Balance on hand.....	\$195.62

A report was received on Alum Specifications from a subcommittee of the Committee on Standard Specification and Methods of Analysis. This report will be published later.

The following officers were then elected:

Chairman, George P. Adamson; *Vice-Chairman*, H. E. Howe; *Secretary*, S. H. Salisbury, Jr.; *Officers, ex-officio*, M. C. Whitaker, *ex-officio*, W. F. Hillebrand, C. H. Herty, C. A. Catlin, David Wesson, H. C. Porter.

Participants in discussions of the papers read were the following: Percy H. Walker, A. H. Sabin, Wm. H. Walker, Wm. Brady, N. A. Dubois, G. W. Gray, W. F. Hillebrand, W. A. Noyes, H. C. Porter, A. H. White, Dr. Smith, Mr. Dickinson, I. M. Bregowsky, G. A. Burrell, A. W. Browns, G. W. Gray, E. S. Merriam, and others.

On Friday morning, Dr. W. F. Hillebrand gave a talk on the Composition of the Bureau of Standards Sheet Brass which caused considerable discussion after which the division adjourned.

S. H. SALISBURY, JR., *Secretary*

RUBBER CHEMISTRY SECTION

After the transaction of the usual business, and the rendering of the program, reports were read by the Specification Committee, the Analytical Committee, and the General Rubber Consideration Committee. After discussion the above reports were approved.

The Analytical Committee was instructed to compile and present to the Executive Committee methods of procedure for determinations commonly made in rubber analyses. The Executive Committee was given power to act on such a procedure within its discretion.

The Executive Committee was instructed to appoint a committee to investigate and report with recommendations on the Physical Testing of Rubber and Compounds. This Committee was given power to act within its own discretion.

It was decided (1) to ask the members of the Rubber Section to contribute \$1.00 each for the purpose of defraying the expenses of the Section; (2) to request the Council of the American Chemical Society to reappoint or retain in office the present officers of the Rubber Section.

After the reading of papers, a vote of thanks was extended to Mr. Savage for his excellently prepared paper on "Some Refinements of the Ignition Method for the Determination of Rubber in Vulcanized Goods."

DORRIS WHIPPLE, *Secretary*

COMMITTEE REPORTS—FERTILIZER CHEMISTRY DIVISION

COMMITTEE ON PHOSPHORIC ACID

This report is supplementary to the report of this Committee published in *THIS JOURNAL*, 3, 118. The latter showed that it was possible for the analyst to prepare an ammonium citrate solution which would give the same results as those obtained from a standard citrate prepared by Mr. Jones of this Committee. However, when a comparison was made with other analysts, the differences in some cases were quite large.

The Committee then endeavored to pick out those factors which would most likely influence the insoluble. That the time of filtering had evidently influenced some of the results was evidenced by the fact that the time varied from five minutes to two and one-half hours, this in a sample of complete goods. Another factor was the use of the volumetric method without checking against the gravimetric.

In order to eliminate these factors as far as possible, the following changes were made in the instructions:

(1) In case of complete goods; after insoluble has been placed on filter and flask washed, fold paper containing insoluble in half and transfer to another funnel.

(2) A standard sample in which the Committee had determined the total phosphoric acid was sent with the other samples.

With these exceptions the instructions were the same as those published in *THIS JOURNAL*, 3, 118.

RESULTS OBTAINED BY THE PHOSPHORIC ACID COMMITTEE OF THE A. C. S.
ON THE STANDARD SAMPLE

All Determinations were Made by the Official Gravimetric Method

Analyst	Total P ₂ O ₅	Average
W. J. Jones	3.85 (a)	3.87
	3.88	3.94
	3.95(b)	
	3.92	
F. D. Fuller	3.90(a)	3.89
	3.90	
	3.86	
C. Farnham	3.86(b)	
	3.92	
	3.86	
	3.89	3.88
J. Q. Burton	4.00	
	3.97	3.99
Maximum		4.00
Minimum		3.86
Average		3.91

(a) Sol. made with H₂SO₄ + HgO.(b) Sol. made with 3 HCl + 1 HNO₃.RESULTS BY OTHER ANALYSTS
Volumetric Method Used throughout unless Otherwise Stated

Sample Analyst	Insoluble P ₂ O ₅		Total P ₂ O ₅	Time for filtering and washing	
	1 Acid phosphate	2 Complete		Minutes	
1.....	0.55	3.15	3.89	1	2
	0.50	3.10	3.86 (g)	2	2
	0.55	3.28
	0.50	2.98
	0.50	3.10 (a)	...	2	2
	0.48	3.05
2.....	0.67	3.63	3.89
	0.67	3.62	3.91 (e)	20	40
	...	3.64	3.89
3.....	1.12(i)	1.54(i)	3.86(g)
4.....	0.60	3.90	3.93	20	28
5.....	0.51	3.42	...	2	4
	0.54	3.62
	0.55	3.52(c)	...	5(c)	...
	0.55	3.54
	...	3.42
6.....	0.59	3.33	...	3	3
	0.52	3.40
	0.56	3.33
7.....	0.57	2.94
	0.57	2.88
8.....	0.32	3.02	4.02
	0.37	3.22	4.05	12	15
	0.37	3.00	3.97
	0.35	3.00 (b)
9.....	0.66	3.92
10.....	0.81	2.68(i)	...	2	5
11.....	0.48	2.94	4.04
	0.49	2.95	4.01	15	20
	0.51	2.88	4.00
	0.49	3.08	3.92
	0.51	3.19 (b)	3.98
	0.48	3.20	3.94
	3.85
	4.29
	4.23 (hg)

SUMMARY OF AVERAGES OF INDIVIDUAL ANALYSTS

Maximum....	0.81	3.92
Minimum....	0.37	2.91
Average.....	0.58	3.39

(a) Citrate sol. prepared by method in *THIS JOURNAL*, 1, 618. Sol. contained 186.3 grams citric acid per liter. Committee method citrate contained 197.4 grams citric acid per liter.

(b) Filtered on funnel with platinum cone.

(c) Filtered and washed without transference.

(e) Silica not removed; allowed to stand two hours in ice water.

(f) Silica removed by dehydration; stood at room temperature over night.

(g) Gravimetric method.

(h) Silica not removed; stood over night at room temperature.

(i) Not included in average.

The variation in the results on acid phosphate is almost exactly the same as that of the previous year. In the case of complete goods the variation has been lowered from one and a quarter to one per cent.

The length of time of filtration has been very materially cut down; some analysts say, however, they can see no advantage that the Hirsch or Buchner funnel has over the glass funnel with platinum cone, providing care is taken not to transfer any of the insoluble matter onto the filter until several washings with hot water have been effected.

The Committee thinks that this work should be continued along these lines with the hope that a suitable method may be worked up which will give more concordant results.

COMMITTEE ON PHOSPHORIC ACID

J. Q. BURTON
W. J. JONES
J. R. POWELL
G. FARNHAM, *Chairman*

COMMITTEE ON PHOSPHATE ROCK

The Committee on Phosphate Rock continued their investigations during the past year. Three sub-committees were appointed to take charge of the different determinations—moisture, iron and alumina and phosphoric acid. The only report received, however, was from the sub-committee on phosphoric acid. A brief abstract of this report is as follows: "The work of the sub-committee on phosphoric acid for 1913, was done by members of the committee and a few other analysts on a sample prepared by mixing together four different kinds of phosphate rock including Tennessee brown and blue, South Carolina and Florida rock. The sample was prepared by mixing the finely ground individual samples, each of which had been previously passed through a 100-mesh sieve. The samples, with instructions, were sent out to eleven analysts, and reports were received from seven, including results in two case from two analysts each, some of the members of the committee and some of the other analysts referred to being unable to find time for this work. The results received varied so widely that your committee considers it inadvisable to average them. As the results began to come in it seemed probable that the wide variations showing up might possibly be laid to the difference among the samples themselves rather than to differences between the analysts. An investigation made with two remaining samples seemed to bear this out, and your committee inclines to the opinion that the sample sent out was not suitable for this work, and that the same work should be repeated on a sample made up of only one type of rock, and that this point be carefully observed in the making up of any future samples. Aside from this point, there is no definite tendency apparent either in the direction of abnormal results by any one of the methods tried by all of the analysts or by any one of the analysts in all of the methods tried."

The announcement published in the *Industrial Journal* in the early part of the year of a tentative standard of phosphate rock having been adopted by the committee, has resulted in a surprising number of requests. Nearly all of the laboratories interested in the fertilizer work in this country as well as in some other countries have been supplied with this sample.

COMMITTEE ON
PHOSPHATE ROCK

W. D. RICHARDSON
S. W. WILEY
C. F. HAGEDORN
W. P. HEATH
F. B. CARPENTER, *Chairman*

COMMITTEE ON FERTILIZER LEGISLATION

Your committee have, during the past year, endeavored to keep up with the new legislation in the various states and used their influence as far as possible to prevent unwise or unjust enactments, but as to bringing about a uniformity of laws they have

been able to accomplish very little; in fact there is less uniformity at the present time than there was a few years ago. In this connection I have considered it desirable to review briefly some of the efforts which have been made towards bringing about uniform laws in the different states.

As far as I can learn from the records, the first fertilizer law in this country worth considering was enacted by the Massachusetts Legislature in 1866; this proved inadequate for the reason that there was no provision for its execution and was amended in 1873, in which form it remained for a number of years. This served as a model for other states and we find in the early laws a striking similarity to the Massachusetts law. In the subsequent years additions and changes have been made so that at the present time the laws in the different states are far from uniform. This lack of uniformity does not lie so much in the general principles of the law, but rather in the elaboration of these principles and the mode of expressing the details.

The Association of Official Agricultural Chemists, recognizing the disadvantages of having the laws unlike in different states, not only from the standpoint of inspection and analysis but also on account of the hardships imposed on the manufacturers, appointed a committee "on uniform methods of fertilizer control." A like committee was also appointed by the "Association of American Agricultural Colleges and Experiment Stations." These committees did a considerable amount of work on the subject and finally after consulting with manufacturers drew up a statement of principles which was quite satisfactory to all parties concerned and made a report to the Association of Official Agricultural Chemists at their Annual Meeting in 1897. This committee was continued as a standing committee, taking up different phases of fertilizer laws, including questions relating to national legislation, reporting annually to the association.

In 1909, the committee presented to the Association, for their endorsement, a proposed form of National Fertilizer law. This, however, did not meet with their approval, it appearing that there was no necessity for such a law as the different states were prepared to attend to the inspection work in a satisfactory manner. On a motion of the chairman the committee was discharged and since that time there has been no Committee on Fertilizer Legislation either in the Association of Official Agricultural Chemists or the Association of American Agricultural Colleges and Experiment Stations.

At the organization of the Fertilizer Division of the American Chemical Society a Committee on Fertilizer Legislation was appointed, which has used its influence against the passage of unwise and unjust laws, but has been unable to accomplish much along the lines of uniform fertilizer legislation. The National Fertilizer Association maintains a legislative committee and points out in their last report the futility of hoping for the adoption of a uniform fertilizer law by the various states as illustrated by the fact that not a single state has taken the law proposed by the Association of Official Agricultural Chemists as a basis of revision.

The most that has been accomplished along the line of uniformity was effected when, about fifteen years ago, some ten of the southern states practically agreed on a uniform law, which was framed by the state chemists and Commissioners of Agriculture in an Association known as the Cotton States Association of Commissioners of Agriculture. Since this time, however, these states have so modified and amended their laws that there is, at the present time, no more uniformity than in other parts of the country.

From the efforts which have been made and the results attained it would appear that there is little hope of ever having a uniform fertilizer law which will be effective in the different states. The question of federal legislation has been suggested as a means of bringing the individual states in line, it being argued that if a model law were passed by Congress there would

be little difficulty in having this enacted by the different states. If this could be effected there is no doubt that manufacturers would favor federal legislation, but there are so many obstacles to be overcome and so much doubt of ultimate success that they prefer to let the matter stand as it is rather than to take chances in having additional complications in the already complex system of legal requirements, which applies especially to those who do an interstate business.

Notwithstanding the fact that there appears to be no hope of uniform laws there is no doubt that the various committees and organizations, which have been referred to, have done much to bring about reasonable legislation as well as to maintain some points in common in different state laws. It is to be regretted that any of these committees have been discharged, especially that of the Association of Official Agricultural Chemists, and I hope at their next meeting a standing committee may be appointed to direct our law-makers when a change in the state laws is contemplated. Many fertilizer bills which are presented to the legislatures are drawn by parties who have no knowledge of the fertilizer business or the necessary requirements to safeguard the interests either of the manufacturer or consumer. Often these bills are prompted by some personal grievance and if enacted would work hardships on both manufacturer and consumer. It is important, therefore, for those who are interested in fair and impartial legislation and in enactment of uniform laws to work together in an effort to bring about the desired results. Our laws are enacted for the protection of both producer and consumer and it is the duty of our agricultural departments to use their influence, as far as possible, in behalf of fair and impartial legislation.

While it may appear that our committee and the other committees, which have been mentioned, have accomplished little in bringing about uniformity, under the existing conditions, it is only through organized effort that anything can be accomplished and I am not only strongly in favor of maintaining a standing committee in our division, but also of urging the appointment of similar committees in the organizations interested in the welfare of the fertilizer manufacturing and agricultural industries.

F. B. CARPENTER, *Chairman*

AMERICAN CHEMICAL JOURNAL TO BE COMBINED WITH THE JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

The Directors of the American Chemical Society have entered into an agreement with Dr. Ira Remsen, Editor of the *American Chemical Journal*, whereby, at the completion of its fiftieth volume, the *American Chemical Journal* will be discontinued as a separate publication and will be incorporated from January, 1914, with the *Journal of the American Chemical Society*.

'AMERICAN PETROLEUM SOCIETY

The American Petroleum Society was organized September 1904, at the Experiment Station of the U. S. Bureau of Mines, Pittsburgh, Pa. This organization is the result of an effort of the Bureau for the past seven years to bring together the men interested in the petroleum industry.

Invitations were sent out in July to the secretaries of twenty-four of the great National Societies of the United States, inviting them to be present and coöperate in this organization. Eighteen of these societies responded at a meeting on August 1st at the Bureau of Mines. A similar invitation was sent out in August to eight additional societies, making a total of thirty-two societies that were invited to attend the September conference. A large number of these were represented when the final organization was completed.

This society will concern itself with the study of all phases of natural gases and petroleum, including the origin, statistics,

conservation, drilling methods, production, transportation, storage, refining and specifications for refined products.

When it is considered that each year, within the United States alone, there is produced crude petroleum and natural gases having a value in excess of \$200,000,000, it is reasonable to suppose that the future of this society is assured. There is to-day a tremendous waste of natural gases which, by proper methods of drilling, could be prevented. Also there is a great waste of crude oil itself by improper methods of production, since in the fields producing paraffin oils the paraffin is allowed to congeal around the well, sealing in the oil strata and thus preventing the recovery of the oil. The necessity for a critical study of petroleum and gas production and conservation is evident.

At the meeting on September 10th at the Bureau of Mines the constitution and by-laws were adopted, and officers were elected as follows:

President, C. D. CHAMBERLAIN, National Petroleum Association, Cleveland, O.

Vice-President, R. GALBREATH, Independent Oil and Gas Producers Association of Oklahoma, Tulsa, Okla.

Secretary, IRVING C. ALLEN, U. S. Bureau of Mines, Pittsburgh, Pa.

Treasurer, WARREN C. PLATT, Independent Petroleum Marketers' Association, Cleveland, O.

Acting Past President, FRANK B. FRETTER, Western Petroleum Refiners' Association, Coffeyville, Kan.

EXECUTIVE COMMITTEE

RALPH ARNOLD, Los Angeles, Cal.

C. F. CLARKSON, Soc. Automobile

Eng., N. Y.

G. M. SWINDELL, Chamber of Mines and Oil, Los Angeles, Cal.

EDMUND O'NEILL, Univ. of Cal., Berkeley Cal.

E. B. RICH, Gasoline Producers' Assoc., Parkersburg, W. Va.

GEO. H. TABER, Gulf Refining Co., Pittsburgh.

The first annual meeting will probably take place in the spring of 1914, and the second annual meeting will be held at the Panama Pacific Universal Exposition in San Francisco in 1915. At the 1915 meeting it is hoped that all the petroleum societies in the country will meet in one great congress where many things of interest and of value will be presented.

An official invitation has been sent from the president of the Exposition at San Francisco to the president of the International Petroleum Commission, which convenes in January, 1914, in Bucharest, Roumania, to hold its annual meeting for 1915 in San Francisco. Plans are already being formulated for this great 1915 meeting, which will be part of the great assembly of the petroleum industries of America, where the foremost petroleum technologists and scientists of the world will congregate.

OBITUARY—JULIUS LEWKOWITSCH

Dr. Julius Lewkowitsch, consulting and analytical chemist and chemical engineer, of London, England, died September

16th at Chamonix, Switzerland, after only a brief illness. Dr. Lewkowitsch was born at Ostrovo, Prussian Silesia, in 1857.

After a brilliant university career at Breslau, he graduated as Doctor of Philosophy. He carried out a considerable quantity of original investigation under Professor Victor von Richter at Breslau. Afterwards he took a position under Professor Hans Landolt in the Chemical Laboratory of the Berlin Agricultural High School, and later was assistant to Professor Victor von Meyer in the University of Heidelberg. During these early years he published much original experimental work on stereochemistry, which was at that time a new and undeveloped subject.

Dr. Lewkowitsch went to England about 25 years ago and, becoming naturalized, took up the study of the industrial technology of fats and oils. By assiduous labor he achieved the position of one of the foremost authorities on vegetable and animal fats and oils. A large number of processes which are widely employed in the utilization and valuation of these important raw materials were devised by him, and his writings on these subjects are regarded as standard works of reference. He also won a considerable reputation as a chemical engineer, while his linguistic attainments were truly remarkable, for he could converse fluently on scientific subjects in most current European languages. These gifts were placed unstintingly at the service of the various scientific societies to which he belonged.

Dr. Lewkowitsch was a fellow and a past member of the Council of both the London Chemical Society and the Institute of Chemistry, and a past member of the Council of the Society of Public Analysts. He was a vice-president and at the time of his decease honorary foreign secretary of the Society of Chemical Industry. He had acted with conspicuous success as chairman of the London Section of this Society and was one of the most active members of the Society's Publication Committee.

He published numerous papers (over 120) on oils, fats and waxes during the last thirty years. His "Chemical Technology and Analysis of Oils, Fats, and Waxes" has passed through four editions as well as appearing in German and French. The first volume of the fifth edition was published on Sept. 4, 1913, and the remaining volumes are now in the press. He also wrote a "Laboratory Companion to Fats and Oils Industries" (English edition, 1901, German edition, 1902), the article "Oils and Fats" in "British Encyclopaedia," and articles on various oils, and fats in Thorpe's "Dictionary of Applied Chemistry."

Dr. Lewkowitsch found his chief recreation in mountaineering, being particularly attached to the Swiss Alps among which he died. He was married in 1902, and is survived by his widow, a son and a daughter.

NOTES AND CORRESPONDENCE

ON THE INFLUENCE OF THE RATIO OF LIME TO MAGNESIA ON PLANTS

Editor of the Journal of Industrial and Engineering Chemistry:

IN THIS JOURNAL, 5, 564, a second article by P. L. Gile and C. N. Ageton appeared concerning the lime-factor, but no convincing evidence was brought forward to show that my objections (THIS JOURNAL, 5, 257) to their first article would not be tenable. In New York, last October, I received full information about the calcareous soils near Ponce from Mr. Ried, former auditor of the Guanica Co. in Porto Rico. He stated that these soils must receive a very heavy dressing of pen manure in order to produce a moderate harvest of cane. Also the proprietor of the Mercedita Cane plantation near Ponce stated to me, on inquiry by letter, that his cane soil receives heavy doses of pen manure. Pen manure, however, is relatively rich in lime and magnesia.

As regards the pineapple plant, it is a lime-loving plant in Florida, but even if it would not be so in other countries this plant can precipitate the excess of lime absorbed abundantly as oxalate. I would like to know those gramineae which can accomplish that in the same measure as pineapple or citrus. I have never stated that soils with a very unfavorable ratio of lime to magnesia should be corrected to the standard ratio, but I have repeatedly pointed out that such soils should be improved by adding one or the other as the case may demand, as far as practicable. See *Landw. Jahrbucher*, 1910, 1008.

I have further never stated that the lime-magnesia ratio in the soil would also be found in every part of the plant. It is a well established fact that seeds show a ratio of mineral nutrients quite different from that of leaves. In seeds, the amount of magnesia exceeds that of lime while in leaves just the reverse

condition is observed. On such determinations see also a communication of mine in the *Landw. Jahrbucher*, 1912, 186.

For the general information of the reader I may be allowed to add the "General Conclusions" to which *Dr. Augustus Volcker*, of the Woburn Experiment Station, near London, has arrived in several years' study on the question of the lime factor. In his recent report on his experiments to the Royal Agricultural Society of England (London, John Murray, Albemarle Street, W. 1913) his conclusions are:

1. That magnesia may, with advantage to the wheat plant, be added to a soil poor in magnesia, so long as the amount of magnesia in the soil does not exceed that of lime.
2. That, as the ratio of lime to magnesia approaches 1 : 1 a benefit will continue to accrue, but that if magnesia be in excess, a toxic influence will be exercised and the crop be diminished.
3. The soils in which magnesia is in excess of lime will not give fully satisfactory results as regards corn growing, but will be benefited by the addition of lime.
4. That lime used in excess does not possess the toxic influence which magnesia, similarly used, has.

These conclusions agree perfectly with those of my co-workers and myself, of *Bernardini* and his co-workers, *Warthiadi*, *Portheim* and *Samec*, and *Hansteen*.

OSCAR LOEW

HYGIENIC INSTITUTE, MUNICH, GERMANY
September 8, 1913

NOTE ON DETERMINATION OF FAT IN ICE CREAM

Editor of the Journal of Industrial and Engineering Chemistry:

In *THIS JOURNAL*, 5, 786, there appears a rapid method for the determination of fat in ice cream, by Mr. H. F. Lichtenberg.

The method appears to be practically the same as one developed by Prof. H. E. Ross, of the Department of Dairy Industry, of the New York State Department of Agriculture, at Cornell University, and published in the *New York Produce Review and American Creamery*, December 28, 1910, and republished by the same paper in a recent issue, the only special difference in the two methods being that Mr. Lichtenberg uses a little more acetic acid and a little less sulfuric acid than originally advised by Prof. Ross. According to the date of publication, it appears that Prof. Ross first developed the method.

HUGH C. TROY

N. Y. STATE COLLEGE OF AGRICULTURE
CORNELL UNIVERSITY, ITHACA
September 24, 1913

DESIGN OF SURFACE COMBUSTION APPLIANCES—CORRECTION.

In my article printed under the above title, *THIS JOURNAL*, 5, 801, the section "That this statement" (bottom of p. 824) to the end of the paragraph should be omitted, and the following discussion substituted for it:

"That this statement is justified is indicated by the following, assuming the inefficient fan and motor that costs 0.9 cent per hour to operate is replaced by a better set, more suitable in size and design. If the service of a standard 15 cubic foot Bunsen top burner is equal to a 10 foot surface combustion burner (ratio 1.5) the gas saving is 5 cubic feet per hour, which is worth $5 \div 1000/100 = 0.5$ cent per hour. If the range had four top burners, one jumbo and two broiler oven burners, and the ratio 1.5 applied to the whole consumption, then for the Bunsen range the hourly gas would be $(3 \times 15) + (3 \times 20) = 105$ cubic feet, against $(3 \times 10) + (3 \times 13.3) = 70$ cubic feet for the surface. For this gas the latter would require $6 \times 70/60 = 7$ cubic feet per minute at 4 inches water pressure. This corresponds to an air horse power of $4 \times 5.2 \times 7/33000 = 0.0044$. With a fan efficiency of 50 per cent the motor horse power is $0.0044/0.5 = 0.0088$, and for 75 per cent motor efficiency the electrical horse-

power input is $0.0088/0.75 = 0.0117$. This is equivalent to $0.0117 \times 746 = 8.76$ watts which at 10 cents per 1000 is worth 0.0876 cent. Thus the electric cost for the whole range is only 0.0876 cent per hour while one top burner saves in gas 0.5 cent per hour. This shows how conservative is the general estimate above, that the gas saving at one burner will more than defray the expense for current for the entire range, for under the conditions named the gas saving at one burner is five times the cost of current for all of them. The vacuum cleaner fan used on the first range consumed ten times the current that was really necessary, yet even so, two top burners save enough gas to pay for all the current."

CHARLES EDWARD LUCKE

October 20, 1913

NOTE ON QUANTITATIVE DETERMINATION OF ROSIN IN PAPER

Editor of the Journal of Industrial and Engineering Chemistry:

I have read with much satisfaction Mr. C. Frank Sammet's paper on "Quantitative Determination of Rosin in Paper," *THIS JOURNAL*, 5, 732.

In order to extract all the rosin present, it is necessary to set free all the combined rosin, a part of which is in combination with the basic cellulose hydrate and a larger part with the base of the alum used.

Instead of using an acidified mixture of alcohol and ether of about 83 per cent which will partially dissolve out on extraction any substances soluble in water, from which the rosin must later be separated by evaporation and extraction with ether, as Mr. Sammet proposes, I prefer to cut the paper for test into strips and wet them out in a very weak solution of hydrochloric or acetic acid. I then air-dry them and place in Soxhlets and extract with absolute alcohol, when the extract may be evaporated and weighed. The extract will be free from water-soluble impurities and give very satisfactory results. Alcohol is the normal solvent for rosin and I prefer it to ether for this work. My suggestion shortens the process and is equally accurate.

MARTIN L. GRIFFIN

RUMFORD, MAINE
September 24, 1913

PLATINUM PRODUCTION INCREASES

While the high price of platinum in the United States in 1912 encouraged prospecting for this rare metal, the production in that year was but slightly larger than that of the preceding year. According to David T. Day, of the United States Geological Survey, in an advance chapter from Mineral Resources for 1912 on the production of platinum and allied metals, the output of crude platinum in 1912 was 721 ounces, compared to 628 ounces in 1911. With the exception of a small yield from the New Rambler copper mines, in Albany County, Wyo., the entire domestic production came from California and Oregon. The greater part of the California platinum was obtained as a by-product in gold dredging in Butte, Yuba, Sacramento, and Calaveras counties.

The United States supply comes chiefly from the unmanufactured and manufactured platinum imported indirectly from Russia. In addition, 45,280 ounces of platinum sand were imported into the United States in 1912 which, by the usual estimate of 80 per cent fine metal, would yield 36,224 ounces of refined platinum. In all, the refined platinum produced in domestic refineries from both domestic and foreign sources amounted to approximately 38,029 fine ounces, valued at \$1,732,221, compared with 29,140 fine ounces similarly obtained in 1911. The total value of our platinum importations in 1912—both raw material and manufactured products—was \$4,503,682 against \$4,866,207 in 1911.

BOOK REVIEWS

Electro-Plating and Analysis of Solutions. By HERMAN H. REAMA. 12mo., 101 pp. The Metal Industry Print, New York. Price, \$5.00.

This book is evidently intended by an electro-plater as a help to others in the same line of business.

Science does not enter into the make of it to any great extent which is unfortunately the case with many other books on the same subject. In the actual description of plating operations such as nickel or copper, the author gives the composition of the baths and leaves the reader to find out elsewhere how to use them, no mention being made of current density, time of plating, or character of the metal deposit with which he is working.

The author's statements often leave much to be desired in the way of clearness as the following passage on conductors, page 2, shows: "It has been stated by competent and qualified people that using bus-bars of the type shown in Fig. 1 (rectangular) will give better service than the ordinary round bar. This is strictly a matter of opinion and is still up to the man in charge or in ownership of the said factory or shop. As heretofore stated, many means of operating can be and are used at the present writing, and it is quite difficult to meet all requirements and all classes of trade and still meet the approval of the majority. Nevertheless, facts are facts, and the above are true."

In the analyses of solutions we find that sulfuric acid is determined in an acid copper sulfate solution by titration with standard alkali, using methyl orange as indicator.

The book is illustrated by cuts from catalogues of various apparatus used in electro-plating establishments with no explanations of their use.

The price of \$5.00 is charged for this book of which there are 101 pages in all, with very little to the page; in fact it is rather absurd to call it a book at all, and it seems to us as if 30 cents would be a high price to pay for it.

SAMUEL A. TUCKER

General Index to the Chemical News, Vols. 1 to 100 (1860-1909). Pp. viii + 712. Price, \$10. Chemical News Office, 16 Newcastle Street, Farringdon Street, London, E. C.

This index covers all material in the issues of *Chemical News* for the first fifty years and should be of inestimable value to every working chemist, whether a subscriber to *Chemical News* or not. The plan of the index, as explained in the preface, is comprehensive yet quite simple and examination shows that, indeed, "every effort has been made to enable readers to find quickly and easily any subjects which have appeared." It is to be hoped that the immense amount of labor involved in the preparation of this reference volume will be appreciated by those for whose benefit it has been prepared.

LEOLA E. MARRS

Calcium Cyanamid. By E. J. PRANKE. Price, \$1.25. The Chemical Publishing Co., Easton, Pa.

There can be no doubt that the use of artificially prepared "fertilizers" for the management of soils and control of crop production is rapidly increasing and must continue to increase. It is also apparent that to maintain an adequate supply of nitrogen carriers, "fixation" of atmospheric nitrogen is a quickly coming necessity. This condition is the main stimulus to pronounced activity in research and invention which is bringing to light various processes or suggestions of immense interest and importance to the scientific and technical world alike. It is not yet possible to predict with any great assurance or conviction what processes are ultimately going to survive the test of experience. So far, the production of calcium cyanamid probably outranks commercially all the nitrogen fixation processes yet tried. Over a dozen factories abroad are now producing the material and at Niagara Falls there is an important plant

whose annual capacity has recently been raised from 25,000 to 50,000 tons. Calcium cyanamid has, moreover, other possible commercial uses than as a fertilizer.

The adoption of this material as a fertilizer by the manufacturer and farming public has on the whole been rapid, and its place is now assured, pending the possible introduction of a satisfactory nitrogen carrier more cheaply prepared. But its present position has not been won without a struggle, with attendant controversies, sometimes acrimonious, which have had good fruit as well as bad, however, in stimulating study and investigation so that now a fairly large body of information exists regarding the chemistry of the substance.

In the volume before us, Mr. Pranke has brought together the main facts that have been established in a systematic arrangement. His attitude toward the value of this material as a fertilizer in comparison with nitrates and ammonium salts impresses the reader as being decidedly biased in spite of an evident effort to maintain a judicial attitude. Nevertheless, he has produced a very interesting and readable book, and a very valuable one, in which even the expert and specialist will probably find new material. The proof-reading seems to have been carelessly done in some parts of the book.

The meagreness of detail in describing the actual technique of manufacture is a disappointment, justified only by the well-known but mistaken policy of manufacturers in maintaining secrecy regarding their factory practice. And to the reviewer the discussion of the effect of soil zeolites and colloids appears unsatisfactory and unconvincing. The very doubtful assumptions as to the presence and the particular properties of these hypothetical substances are not necessary to explain the phenomena of surface action in soils, and invoking their aid, a common practice these days among soil chemists in difficulties, merely makes against clear thinking.

FRANK K. CAMERON

The American Fertilizer Handbook. 1913 Ed. 356 pp. Price, \$1.00. Ware Bros. Company, 1010 Arch Street, Philadelphia.

It would be difficult to estimate the service rendered to those interested in fertilizers by these annual handbooks. This particular issue contains four noticeable sections:

(1) A very comprehensive advertising section, consisting of a classified directory of the allied fertilizer trades including manufacturers of fertilizer machinery and factory equipment; manufacturers of and dealers in fertilizer materials and supplies; brokers, importers and exporters, chemists, phosphate miners, sulfuric acid plants, etc.

(2) Directories of the cottonseed oil mills and of the fertilizer manufacturers of the U. S.—arranged by states.

(3) Valuable tables, such as sulfuric acid and fertilizer formulae tables; a list of agricultural experiment stations; an annual review of the fertilizer materials market, etc.

(4) A series of interesting and instructive articles on special topics, prepared by experts especially for this volume. These include: "Fertilizer Materials in the U. S.," Frank K. Cameron; "The Year's Progress in the Fixation of Atmospheric Nitrogen," T. C. Pinkerton; "Middle West Soil Improvement Committee," H. G. Bell; "The Menhaden Industry," J. W. Turrentine; "Some Analyses of Fish Scrap," J. R. Lindemuth and E. G. Parker; "Sampling of Fertilizers," J. S. Brogdon; "The Sulfuric Acid Industry," A. M. Fairlie; "Fertilizers for Hay and Pastures," E. B. Voorhees; "Cyanamid," E. J. Pranke; "Definitions of Fertilizer Materials," T. C. Pinkerton; "The Chicago Ammoniate Market," J. B. Sardy; "On Tennessee Phosphate Mining Practice," L. P. Brown; "Florida Phosphate Rock—1912," E. H. Sellards; "Production of Phosphate Rock in 1911," F. B. Van Horn.

LEOLA E. MARRS

NEW PUBLICATIONS

By D. D. BERGZIMMER, Librarian The Chemists' Club, New York

- Alumina, The Manufacture of.** By A. BERGE. 8vo. 70 pp. Price, \$0.75. M. Knapp Halle. (German.)
- Analysis, Laboratory Manual of Testing Materials.** By WILLIAM K. HAYE and HERBERT H. SCOTFIELD. 8vo. 130 pp. Price, \$1.25. McGraw-Hill Book Co., New York.
- Analysis, Qualitative Chemical.** By WILHELM WELLDAY SCOTT. 8vo. 160 pp. Price, \$1.50. D. Van Nostrand, New York.
- Analysis, Technical Gas and Fuel.** By ALFRED H. WHITE. 8vo. 276 pp. Price, \$2.00. McGraw-Hill Book Co., New York.
- Arsenic Compounds, Organic, Handbook of the.** By A. BERTHEIM. 1. 8vo. 238 pp. Price, \$2.00. F. Enke, Stuttgart. (German.)
- Asphalts, Natural Rock, and Bitumens.** By A. DANLEY. 8vo. Price, \$2.50. D. Van Nostrand Co., New York.
- Cellulose, Production of, for Paper Manufacture other than those from Wood.** By HENRY DE MONTESSEUS DE BALLOIRE. 8vo. 294 pp. Price, \$2.50. Bernard Tignol, Paris.
- Cement, Portland, its Manufacture, Testing and Use.** By D. AND B. BUTLER. 3rd edition. 8vo. 470 pp. Price, \$4.00. Spon & Chamberlain, London.
- Chemistry, A New Era in.** By HARRY C. JONES. 8vo. 326 pp. Price, \$2.00. D. Van Nostrand Co., New York.
- Chemistry, Textbook of.** By WILLIAM A. NOYES. L. 12mo. 602 pp. Price, \$2.25. Henry Holt & Co., New York.
- Chemistry, The Theories of.** By EDGAR F. SMITH. 8vo. 188 pp. Price, \$1.15. John C. Winston Co., Philadelphia.
- Color Chemistry, Textbook of. Vol. I.** By E. GRANDMOUGIN. 4th edition. 8vo. Price, \$3.75. F. Deuticke, Vienna. (German.)
- Coal Tar Dyes and Allied Industries, Progress in the Manufacture of. Part X. 1910-1912.** By P. FRIEDLANDER. L. 8vo. 1422 pp. Price, \$18.75. Julius Springer, Berlin. (German.)
- Dyestuffs, Synthetic, and the Intermediate Products from which they are Derived.** By JOHN C. CAIN and J. F. THORPE. 2nd edition. 8vo. 440 pp. Price, \$5.00. London.
- Electrochemistry, Elements of.** By EDGAR F. SMITH. 8vo. 200 pp. Price, \$0.90. John C. Winston Co., Philadelphia.
- Encyclopedia, New, of Scientific, Technical and Industrial Chemistry. Vol. II.** By I. GUARESCHI. 4°. 1116 pp. Price, \$6.00. Umiore Tip.-Ed. Torinese, Turin. (Italian.)
- Fats, Animal, and Butters.** By ALBERT BRUM. 8vo. Price, \$1.25. Ch. Beranger, Paris. (French.)
- Food, Text-book on the Chemistry of. Vol. II.** H. ROETTGER. 4th edition. 8vo. Price, \$4.00. Johann Ambrosius Barth, Leipzig. (German.)
- Gases, The Influence of Inert, on Inflammable Gaseous Mixtures.** By J. K. CLEMENT. 8vo. 24 pp. U. S. Bureau of Mines, Technical Paper 43.
- Iron Ores, The Titaniferous, in the United States, their Composition and Economic Value.** By JOSEPH T. SINGEWALD, JR. 8vo. 145 pp. U. S. Bureau of Mines, Bulletin 64.
- Kaolin and Feldspar, Mining and Treatment of, in the Southern Appalachian Region.** By A. S. WATTS. 8vo. 170 pp. U. S. Bureau of Mines, Bulletin 53.
- Liquid Air, The Production, Application and Storage of.** By O. KAUSCH. 4th edition. 8vo. 463 pp. Price, \$3.75. C. Steinert, Weimar. (German.)
- Metal Casting.** By ERNST A. SCHOTT. 8vo. 285 pp. Price, \$3.00. Bernhard F. Voigt, Leipzig. (German.)
- Metallurgical Analysis.** By NATHANIEL W. LORD and DANA J. DEMOREST. 3rd edition. 8vo. 330 pp. Price, \$2.50. McGraw-Hill Book Co., New York.
- Mineral Deposits.** By WALDEMAR LINDGREN. 8vo. 882 pp. Price, \$5.00. McGraw-Hill Book Co., New York.
- Minerals, The Useful, with the Exception of Ores, Potash Salts, Coal and Petroleum. Vol. I.** By B. DAMMER and O. TRETZE. 2 vols. L. 8vo. 501 pp. Price, \$4.00. F. Enke, Stuttgart. (German.)
- Nitrogen Industry, The Air.** By A. PERLICK. 8vo. Price, \$1.50. W. Klinkhardt, Leipzig. (German.)
- Oils, Fats and Waxes, Chemical Technology and Analysis of. Vol. I.** By J. LEWKOWITSCH. 3 vols. 5th edition. 8vo. Price, \$6.25. Macmillan & Co., New York.
- Peroxid, Hydrogen, Production of, by the Cathodic Reduction of Oxygen.** By O. PRIESS. 8vo. University of Erlangen. (Dissertation.) (German.)
- Physico-Chemical Theory, The Application of, to Technical Processes and Manufacturing Methods.** By R. KREMANN. 8vo. 205 pp. Price, \$2.25. Constable & Co., London. (Translation.)
- Plant Products, An Introduction to the Chemistry of.** By PAUL HAYS and T. G. HILL. 8vo. 104 pp. Price, \$2.25. Longmans, Green & Co., New York.
- Rare Earths, Utilization of the.** By C. R. BOEHM. 8vo. Price, \$1.25. Veit & Co., Leipzig.
- Reagents, Merck's Index of Chemical.** By MERCK & Co. 3rd edition. L. 8vo. 446 pp. Julius Springer, Berlin. (German.)
- Rubber, The Chemistry of.** By B. D. PORRITT. Cr. 8vo. Price, \$0.50. Gurney & Jackson, London.
- Spectro-Chemistry, Introduction to.** By G. URBAIN. 8vo. Price, \$2.50. Theodor Steinkopff, Dresden. (Translation.) (German.)
- Steel, The Manufacture of.** By H. NOBLE. 2nd edition. 8vo. Price, \$5.25. Dunod & Pinat, Paris. (French.)
- Sulfur, Colloidal.** By S. ODEN. Let. 8vo. 193 pp. Price, \$4.00. Akademische Buchhandlung, Upsala. (German.)
- Technical Processes and Manufacturing Methods, The Application of Physico-Chemical Theory to.** By R. KREMANN. 8vo. Price, \$2.25. Constable & Co., London. (Translation.)
- Temperature Measurement, Methods of.** By BRUNO THIEME. 8vo. 160 pp. Price, \$1.00. M. Krayn, Berlin. (German.)
- Zinc and Cadmium and their Production from Ores and By-products.** By R. G. MAX LIEBIG. 8vo. 598 pp. Price, \$8.00. O. Spamer, Leipzig. (German.)

RECENT JOURNAL ARTICLES

- Alloy, A New Osmium-Platinum.** By F. ZIMMERMANN. *Chemical Engineer*, Vol. 18, 1913, No. 3, pp. 99-107.
- Asphalt Paving Cements and Road Binders.** By J. W. HOWARD. *Engineering Record*, Vol. 68, 1913, No. 13, pp. 345-347.
- Cellulose, Obtaining, from Wood and Textile Fibers as well as Abolition of the By-product Lyes.** By HASENBACUMER and BRAUN. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 73, pp. 481-485.
- Cement, Composition Flooring.** By H. M. HOOKER. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 6, pp. 305-338.
- Cement Materials and the Manufacture of Portland Cement in Montana.** By W. H. ANDREWS. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 81, pp. 2383-2389.
- Cereals, The Chemical Composition of South African Maize and other.** By C. F. JURITZ. *South African Agricultural Journal*, Vol. 6, 1913, No. 2, pp. 189-197.
- Coke Oven Plant, The Modern, Recovery of By-products in.** By C. A. MEISSNER. *American Gas Light Journal*, Vol. 99, 1913, No. 13, pp. 199 and 202-203.
- Cyanid, Sodium, Manufacture of.** By M. A. VASSEUR. *Revue de Chemie Industrielle*, Vol. 24, 1913, No. 285, pp. 221-226.
- Formic Acid as a Solvent.** By OSSIAN ASCHAN. *Chemiker Zeitung*, Vol. 37, 1913, No. 112, pp. 1117-1118.
- Indicator for Oxidizing Agents, An Electrochemical.** By E. K. RIDEAL and U. R. EVANS. *Analyst*, Vol. 38, 1913, No. 449, pp. 353-363.
- Inorganic Manufacturing Industry, Progress in the, 1905-1912.** By BRUNO WAESER. *Chemiker Zeitung*, Vol. 37, 1913, No. 110, pp. 1097-1098.
- Lime-Nitrogen Industry.** By E. O. SIEBNER. *Chemiker Zeitung*, Vol. 37, 1913, No. 106, pp. 1057-1058.
- Organic Chemistry, The Spectroscope in.** By JAMES J. DOBBIE. *American Chemical Journal*, Vol. 50, 1913, No. 4, pp. 231-243.
- Paper, A New Source of Pulp Supply.** By FREDERICK F. STRONG. *Paper Makers' Monthly Journal*, Vol. 51, 1913, No. 9, pp. 397-399.
- Refractories for the Modern Boiler Plant.** By KERMEITH SEAUER. *Proceedings of the Engineers' Society of Western Pennsylvania*, Vol. 29, 1913, No. 6, pp. 339-362.
- Sewage-Sludge Utilization.** By HERMANN BACK and LESLIE C. FRANK. *Engineering Record*, Vol. 68, 1913, No. 12, pp. 331-333.
- Smoke Prevention.** ANONYMOUS. *Industrial World*, Vol. 47, 1913, No. 37, pp. 1093-1101.
- Steel, Over-Oxidation of.** By W. R. SHIMER and F. O. KICHLINE. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 81, pp. 2361-2377.
- Steel, Volumetric Determination of Phosphorus in, According to Macagno's Method.** By H. WDOWISZEWSKI. *Chemiker Zeitung*, Vol. 37, 1913, No. 107, pp. 1069-1071.
- Tanning Effluents, Valuation and Fixation of.** By J. W. PHELAN and J. H. COHEN. *Journal of the American Leather Chemists' Association*, Vol. 8, 1913, No. 10, pp. 426-438.
- Thermocouples, Base Metal, Some Observations on.** By O. L. KOWALKE. *Chemical Engineer*, Vol. 18, 1913, No. 3, pp. 93-96.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

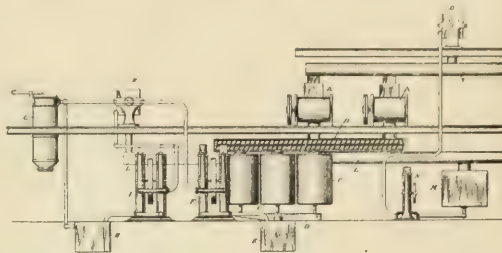
Preparation of Catalytic Substances in a Minutely Divided State. H. Kast, Aug. 12, 1913. U. S. Pat. 1,070,138. Heavy metal salts of the trinitrophenols are heated in a weakly oxidizing atmosphere until the salts burn off by themselves leaving behind their ashes in a very voluminous and spongy form.

Sulfate of Potash and Alumina. H. F. Chappell, Aug. 12, 1913. U. S. Pat. 1,070,324. Sulfate of potassium and aluminum oxide are obtained from natural deposits of alum stone, alum rock and alunite by heating them to a temperature of about 800-1000° C. until the aluminium compounds present are converted into insoluble aluminum oxide and the potassium compounds present are converted into potassium sulfate; the potassium sulfate is separated by lixiviation.

Extracting Oils from Fuller's Earth and Like Materials. L. Felizat, Aug. 19, 1913. U. S. Pat. 1,070,435. Oil is recovered from Fuller's earth and like materials used in refining oils by adding water and a soluble alkaline carbonate to form a fluid mass. This is heated and carbonic gas is then liberated from the carbonate by means of acid to free the oil from the earthy material and permit it to rise to the top of the mass.

Cleaning and Refining Oil. C. W. Stone, Aug. 19, 1913. U. S. Pat. 1,070,555. Free water, emulsified water and oil having a lower boiling point than water are removed from crude petroleum by heating it in a stationary condition to a temperature sufficient to cause the free water to settle. The petroleum is then drawn off and caused to flow rapidly over a metallic surface heated to a temperature above the boiling point of water,

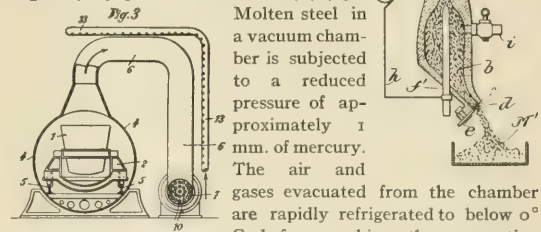
Manufacturing of White Sugar Direct from Raw Sugar-Juices. Wijnberg and Sauer, Aug. 19, 1913. U. S. Pat.



1,070,654. Raw sugar juices are refined by adding about 1 per cent of normal sulfur dioxide. The treated juices are then mixed with decolorizing carbon and kieselguhr, the latter being afterwards removed by filtering.

Granular Carbon. J. C. Lee, Aug. 26, 1913. U. S. Pat. 1,071,442. Finely divided anthracite coal is heated in the apparatus illustrated by means of an electrical current of definite intensity, the particles of coal being controlled so that each particle is exposed to the action of the current for a definite period of time.

Treating Melted Metals, Alloys and Steels. L. M. V. H. Baraduc-Muller, Aug. 26, 1913. U. S. Pat. 1,071,632. Molten steel in a vacuum chamber is subjected to a reduced pressure of approximately 1 mm. of mercury. The air and gases evacuated from the chamber are rapidly refrigerated to below 0° C. before reaching the evacuating apparatus whereby the volume and temperature of the air and gases coming from the vacuum chamber are greatly reduced.

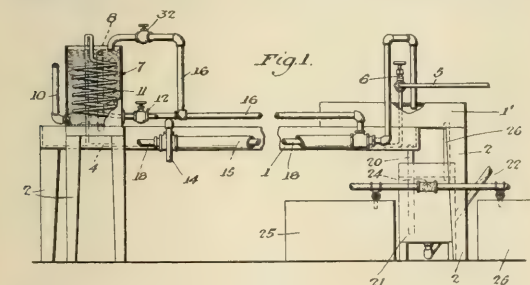


Improving the Condition of Flour. J. A. Wesener, Sept. 2, 1913. U. S. Pat. 1,071,977. Flour is treated with anhydrous chlorine (diluted with an inactive gas) in order to mature and whiten it.

Explosive. F. Raschig, Sept. 2, 1913. U. S. Pat. 1,072,032. The explosive comprises sodium nitrate and the alkali soluble constituents of waste products of the soda pulp process.

Bleaching Solid and Semisolid Fats of All Kinds. F. Richter and L. von Orth, Sept. 2, 1913. U. S. Pat. 1,072,034. The fat is melted and filtered through a layer of aluminium oxide obtained from aluminium amalgam. This oxide is stated to have a much higher absorptive power than aluminium oxide produced by other processes as by heating trihydrate of aluminium. The aluminium oxide after use may be regenerated by calcining.

Potash Salts from Feldspar. H. P. Bassett, Sept. 9, 1913. U. S. Pat. 1,072,686. Feldspar or similar potassium-containing rock is heated to a red heat with one-half its weight of sodium chlorid and the potassium salts thus rendered soluble are extracted with water.



thereby breaking up the emulsion and causing a portion of the water content to separate in a liquid condition and another portion of the water to vaporize together with the volatile oil having a lower boiling point than water. The oil is then allowed to stand to settle out the separated water. The vapors of water and oil arising from the rapidly flowing body of oil are collected and condensed.

Making Oxalates. A. Hempel, Aug. 19, 1913. U. S. Pat. 1,070,806. Oxalates are produced from formates by heating to from 360° to 440° C. in an atmosphere of the waste gas which is produced in the manufacture of formates from carbon monoxid and caustic alkali.

Soluble Barium Salts. F. F. Hunt, Aug. 19, 1913. U. S. Pat. 1,070,810. Soluble barium salts are obtained from residues containing barium in an acid-soluble form by adding a sufficient quantity of an acid to solubilize the acid-soluble barium compounds. The treated residues are then dried and leached with water to obtain a solution of the barium salts.

Explosive. J. F. O'Brien, Aug. 19, 1913. U. S. Pat. 1,070,836. The mixture consists of potassium chlorate, starch and silica.

MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF OCTOBER, 1913

ORGANIC CHEMICALS

Acetanilid.....	Lb.	21	@	23
Acetic Acid (28 per cent).....	C.	1.75	@	1.90
Acetone (drums).....	Lb.	13 1/2	@	14 1/2
Alcohol, denatured (180 proof).....	Gal.	35	@	38
Alcohol, grain (188 proof).....	Gal.	2 50	@	2 52
Alcohol, wood (95 per cent).....	Gal.	46	@	48
Amyl Acetate.....	Gal.	2.20	@	2.30
Aniline Oil.....	Lb.	10 1/2	@	10 1/2
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	21	@	23
Camphor (refined in bulk).....	Lb.	42 1/2	@	44
Carbolic Acid (drums).....	Lb.	8 1/2	@	11
Carbon Bisulfide.....	Lb.	6 1/2	@	8
Carbon Tetrachloride (drums).....	Lb.	7 1/2	@	8
Chloroform.....	Lb.	25	@	35
Citric Acid (domestic), crystals.....	Lb.	55	@	56
Dextrine (corn).....	C.	3.02	@	3.23
Dextrine (imported potato).....	Lb.	6	@	7
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	8 1/2	@	9 1/2
Glycerine (dynamite).....	Lb.	19 1/4	@	20 1/4
Oxalic Acid.....	Lb.	7 1/2	@	7 3/4
Pyrogallie Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	25	@	30
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2.34	@	3.00
Starch (potato).....	Lb.	4 1/2	@	5
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	23 1/2	@	23 1/2
Starch (wheat).....	Lb.	5 1/4	@	6 1/2
Tannic Acid (commercial).....	Lb.	35	@	36
Tartaric Acid, crystals.....	Lb.	31 1/2	@	32 1/2

INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 1/4	@	8
Acetate of Lime (gray).....	C.	2.00	@	2.05
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	57 1/2	@	6 1/2
Aqua Ammonia (drums) 16°.....	Lb.	2 1/2	@	2 1/2
Arsenic, white.....	Lb.	3 1/8	@	3 3/4
Barium Chloride.....	C.	1.67 1/2	@	1.90
Barium Nitrate.....	Lb.	5 1/4	@	5 1/2
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.25	@	1.30
Blue Vitriol.....	Lb.	5	@	5 1/4
Borax, crystals (bags).....	Lb.	3 3/4	@	4 1/4
Boric Acid, crystals (powd.).....	Lb.	7	@	7 1/2
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	85	@	1.10
Chalk (light precipitated).....	Lb.	4	@	4 1/2
China Clay (imported).....	Ton	nominal		
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.55	@	3.60
Lead Nitrate.....	Lb.	8	@	8 1/2
Litharge (American).....	Lb.	6 1/4	@	7
Lithium Carbonate.....	Lb.	65	@	70
Magnesia (powdered).....	Lb.	5 1/2	@	6
Magnesite (raw).....	Ton	30.00	@	35.00
Nitric Acid, 36°.....	Lb.	37 1/2	@	4 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	21 1/2	@	25 1/2
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 1/4	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%.....	C.	3.30	@	3.50
Potassium Chlorate, crystals.....	Lb.	8 1/4	@	9 1/2
Potassium Cyanide (bulk), 98-99%.....	Lb.	19	@	24
Potassium Hydroxide.....	C.	4.00	@	4.25
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	4 1/2	@	5
Potassium Permanganate (bulk).....	Lb.	9 1/4	@	10
Quicksilver, Flask (75 lbs.).....	Lb.	38.00	@	40.00
Red Lead (American).....	Lb.	7	@	7 1/2
Salt Cake (glass-makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	38 1/2	@	40 1/2
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	3 1/4	@	4 1/2
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	2 1/2	@	3
Sodium Bichromate.....	Lb.	4 1/2	@	5 1/2
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	8 1/4	@	9 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	2.32 1/2	@	2.40
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	67 1/2	@	7 1/2
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	12 1/2	@	13 1/2
Tin Oxide.....	Lb.	44	@	45
White Lead (American, dry).....	Lb.	5 1/4	@	6
Zinc Carbonate.....	Lb.	9	@	10
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/2	@	6 1/2
Zinc Sulfate.....	Lb.	2 1/2	@	3

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	42	@	45
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	87 1/2	@	10
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.35	@	6.40
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	42	@	42 1/2
Cottonseed Oil (p. s. y.).....	C.	6.80	@	6.90
Cylindric Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	9	@	9 1/2
Lard Oil (prime winter).....	Gal.	93	@	95
Linseed Oil (double-boiled).....	Gal.	48	@	49
Menhaden Oil (crude).....	Gal.	33	@	35
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2	@	3 1/2
Paraffine Oil (high viscosity).....	Gal.	26	@	28
Rosin ("F" grade).....	Bbl.	4.00	@	4.10
Rosin Oil (first run).....	Gal.	27	@	28
Shellac, T. N.....	Lb.	21 1/2	@	23 1/2
Spermaceti (cake).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	8 1/4	@	9
Tallow (acidless).....	Gal.	63	@	65
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	43 1/2	@	45

METALS

Aluminum (No. 1 ingots).....	Lb.	20	@	21
Antimony (Hallet's).....	Lb.	7 1/2	@	7 1/2
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	Lb.	16 1/2	@	—
Copper (lake).....	Lb.	16 1/4	@	—
Lead, N. Y.....	Lb.	4.35	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	61 1/2	@	62 1/2
Tin.....	C.	40.50	@	43.50
Zinc.....	C.	5.30	@	5.40

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	3.07 1/2	@	3.10
Blood, dried.....	Unit	3.15	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	27.50	@	28.00
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.10
Castor meal.....	Unit	3.30	@	—
Fish Scrap, domestic, dried.....	Unit	3.25	@	3.35 & 10
Mowrah meal.....	Ton	nominal		
Phosphate, acid, 16 per cent bulk.....	Ton	—	@	6.75
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	38.55	@	—
Pyrites, furnace size, imported.....	Unit	0.13 1/4	@	—
Tankage, high-grade.....	Unit	3.12 1/2	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

Volume V

DECEMBER, 1913

No. 12

BOARD OF EDITORS

Editor: M. C. WHITAKER

Associate Editors: G. P. Adamson, E. G. Bailey, H. E. Barnard, G. E. Barton, A. V. Bleining, Wm. Brady, C. A. Browne, F. K. Cameron, F. B. Carpenter, C. E. Caspari, V. Coblenz, W. C. Geer, W. F. Hillebrand, W. D. Horne, T. Kamoi, A. D. Little, C. E. Lucke, P. C. McIlhiney, J. M. Matthews, T. J. Parker, J. D. Pennock, W. D. Richardson, G. C. Stone, E. Twitchell, R. Wahl, W. H. Walker, W. R. Whitney, A. M. Wright.

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly.

Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

Contributions should be addressed to M. C. Whitaker, Columbia University, New York City

Communications concerning advertisements should be sent to The American Chemical Society, 42 West 39th St., New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

Research.....	966
The Control of Public Utilities.....	967

ORIGINAL PAPERS:

The Protection of Iron and Steel by Paint Films. By Norman A. Dubois.....	968
The Oleoresins of Jeffrey and Singleleaf Pines. By A. W. Schorger.....	971
The Hydrocarbons of Utah. By Carlos Bardwell, B. Arthur Berryman, Thomas B. Brighton and Kenneth D. Kuhre.....	973
Winkler's Method for the Determination of Oxygen in Water; the Effect of Nitrite and Its Prevention. By Frank E. Hale and Thomas W. Melia.....	976
Sulfur Dioxide in Gelatine. By Paul Poetschke.....	980
Experimental Data on the Determination of Saccharin in Foods with a Modification of Schmidt's Methods. By Halsey Durand.....	987
Bouillon Cubes. By F. C. Cook.....	989
The Influence of Bran-Extracts on the Baking Qualities of Flour. By H. L. White.....	990
The Analysis of Maple Products, II. A Comparative Study of the Delicacy of Methods. By J. F. Snell and J. M. Scott.....	993
On the Preparation of Neutral Ammonium Citrate Solution. By Paul Rudnick and W. L. Latshaw.....	998
A Study of the Pemberton-Kilgore Method for Determination of Phosphoric Acid. By P. L. Hibbard.....	998
The Composition of Sediments from the Potomac and Shenandoah Rivers. By Joseph G. Smith and William H. Fry.....	1009
Estimation of the Lime Requirement of Soils. By J. A. Bizzell and T. L. Lyon.....	1011
An Interesting Soil Water Question in British Guiana. By Maurice Bird.....	1012
Microorganisms in Commercial Lime-Sulfur. By C. A. Peters and A. W. Brooks.....	1013
The Assay of Individual Plants of <i>Datura stramonium</i> L., <i>Datura tatula</i> L. and Other Species and Varieties. By F. A. Miller and J. W. Meader.....	1014

LABORATORY AND PLANT:

Determination of Nitrogen by the Nitrometer. By C. M. Joyce and Harry La Tourette.....	1017
Laboratory Column Still. By H. K. Benson.....	1018
An Improved Laboratory Burner. By Chas. P. Fox.....	1019

ADDRESSES:

Biochemistry. By Carl L. Alsberg.....	1019
---------------------------------------	------

The Programs for the Sectional Meetings of the American Chemical Society. A Suggestion. By Bernhard C. Hesse.....	1020
Empirical Requirements in Asphalt Specifications. By Leroy M. Law.....	1021

CURRENT INDUSTRIAL NEWS:

Sulfite Waste Liquor Problems.....	1024
Nickel a By-Product in the United States.....	1024
Practical Considerations Affecting Choice of Thermometers in Industrial Plants.....	1024
The Salt Industry of Russia.....	1024
Chemical Trade of Germany.....	1025
Impressions of European Sewage-Treatment Methods	1025
Action of Alkali and Sea Water on Cements.....	1026
Alloys of Aluminum.....	1026
Waterproofing of Concrete Structures.....	1027
Fuller's Earth.....	1028
New Chemical Process for Fiber.....	1028
Sewage Disposal in New York.....	1028
Exhausting Lamp Bulbs at High Temperature.....	1028
Cadmium Storage Battery Plates.....	1028
French Alcohol Production and Uses.....	1029
Natural Gas Used.....	1029
Gold and Platinum by the Ton.....	1029
Production of Platinum.....	1029

NOTES AND CORRESPONDENCE:

Syrian Autoburning Limestone.....	1029
Obituary: Jules Ogier.....	1030
American Institute of Chemical Engineers.....	1030
Ortho-Tolidine as a Reagent for the Colorimetric Estimation of Small Quantities of Free Chlorine—a Correction.....	1030

BOOK REVIEWS:

Industrial and Manufacturing Chemistry: Organic; Chemistry of the Oil Industries; Explosives: A Synoptic and Critical Treatment of the Literature of the Subject as Gathered from Various Sources; Allen's Commercial Organic Analysis; Natural Rock Asphalts and Bitumens; Correction: Liquid Air—Oxygen—Nitrogen.....	1030
---	------

NEW PUBLICATIONS.....	1033
-----------------------	------

RECENT INVENTIONS.....	1034
------------------------	------

MARKET REPORT.....	1036
--------------------	------

AUTHOR INDEX.....	1037
-------------------	------

SUBJECT INDEX.....	1042
--------------------	------

EDITORIALS

RESEARCH

Much progress has been made in recent years in the establishment of research laboratories in the more progressive manufacturing plants in this country; yet a canvass of the situation will show that a comparatively small percentage of industrial managers is even now convinced that a careful scientific study of processes and products will pay, and these managers do not look with favor upon the suggestion that a very small portion of their earnings might with profit be invested in a reserve of knowledge of their industry.

The American manufacturer has found the development of his business so easy and rapid, either on account of favorable raw material conditions, or a greedy demand for his products that it has not been necessary for him to devote attention to the study of more efficient processes, in order to reap enormous profits. In other cases the time and energy of many managers has been so taken up with the problems of keeping up with the natural demands, due to the growth of the country, that a scientific study of the industry has been, and will continue to be, deferred until profits begin to fail.

Probably the greatest factor in retarding the development of scientific research among our industries has been high tariff. This high tariff has caused many of our industries to prosper and pay enormous profits in spite of their short-sighted management. Political research, with a view to exploiting the consumer, is well understood by such managers and it is a regrettable fact that many of them have spent thousands of dollars on the lobby and not one cent for placing their business on a sound scientific footing.

Perhaps the managers who have specialized in this form of political research are the victims of certain economic conditions and should not be held responsible for the selection of this method of building up their business. They are employed to produce a product at a profit and it is not always stipulated by the stockholders or directors how that profit shall be produced. No stockholder has yet been discovered who raises any question as to the source of profits so long as they are large. The relations between the amount of real money invested and the profits accruing therefrom have long since been submerged in water—the universal solvent for excessive profits. The position of the manager under such conditions is truly distressing and blame attaches more to the people and practices which have made it necessary for him to follow the chances for the greatest profits regardless of all ethical considerations.

The recent reductions in the tariff on many products and the removal of that seductive prospect from the field of probability for increasing profits will undoubtedly result in stimulating interest in the scientific study of processes and products as the most likely means of maintaining earnings. The loss of this tariff protection will, in the end, exert a great stabilizing in-

fluence on our industrial development. The protection of industry by flimsy artificial regulations is sooner or later bound to collapse, and the wiser course would be to build upon stronger foundations. It may take some time for manufacturers who have enjoyed tariff protection to realize that relief from their present predicament may come through a more systematic application of research methods but ultimately, after the hope of increasing profits by the political route has been entirely eliminated, they will turn to the scientific method.

The control and use of the immutable laws of nature obviously offer a more stable basis upon which to build and a more uniform source of profit than any structure built upon artificial conditions created by legislation.

The quality of many of our manufactured products is not up to the highest standard, but the demand has been so pressing that the goods have been accepted in spite of their defects. Many concerns spend almost as much time and money in making their goods stay sold as they spend on their manufacture. We all know that it is an occasion for comment and often congratulation when a piece of machinery is delivered which is capable of being put into use without disclosing fundamental defects in design, arrangement, construction or materials. A delivery of supplies which does not occasion complaints, endless correspondence or probably adjustments is a curiosity in some industrial work.

The quality problem is by no means settled in our industries and before we reach the saturation point of our domestic markets and attempt to branch out into foreign trade in competition with the skill and workmanship of other nations, we shall have to solve it. Cut-and-try methods for the design of equipment, which result in such monstrosities as a ten-foot vacuum pan with a four-inch vapor outlet, a machine where the same sized shaft is used throughout regardless of the fact that the working load ratio in different parts of the machine is 45 to 1, and other misfits too numerous and well known to mention, will have to be replaced by scientific methods. The superlative claims of advertising managers and the "talking points" of salesmen, which they often admit are not necessarily points of merit, will avail for a time but the buyer is slowly awakening to the fact that he is buying value and that there is a definite relation between *value* and *price*.

The quality and value of a product are based upon the application of correct principles in its conception, preparation and use, and these correct principles can be established only by scientific investigation. It is difficult to see how substantial progress can be made in this direction without such study.

Many managers take the position that they will not install research laboratories for the purpose of developing their industry because they can purchase

from abroad or elsewhere ready-made improvements and developments without taking the risk of the experimental expenses. This policy is practiced by a number of well-known corporations. Its wisdom may never be determined because it will be impossible to decide, when successful, whether its success depends upon the method or upon superior advantage from other causes. It seems fair to assume, however, that the chances are against successful business administration on this policy. The risk of not finding new developments or of not having an opportunity to purchase them, may result in losses many times greater than the expense of maintaining research departments.

There are problems in industrial work which are common to all industries in a certain field or to a large group of industries in the same field in which coöperation in research would benefit all alike. I refer particularly to such problems as the disposition of wastes from dye-houses, paper mills, gas works, the smoke nuisance problem which is important to all steam power using industries, flue dust from smelter stacks, flue dust from pyrites burners, cement dust from cement mills, etc.

It is easily conceivable that a number of concerns in similar or identical fields might coöperate for the investigation and the development of common problems for the equal benefit of all concerned and probably the salvation of the industry itself. Such coöperation is now being brought about in a measure by the scientific societies and organizations represented in different industries. For example, the Michigan Gas Association supplies funds for the investigation of problems in gas manufacture common to the constituent members of that organization. The American Tanners' Association is conducting investigations common to the tanning industry, and other societies are showing a disposition to coöperate on research problems. Substantial progress on coöperative research will not be made by the technical societies, however, on account of the limited means at their disposal and the comparatively large number and magnitude of the problems.

If industrial concerns were to combine for the support of specific investigations on problems of common interest, great progress might be made. The element of desiring to monopolize all of the results and to enjoy some exclusive advantage over participants because they are business competitors would have to be entirely eliminated and managers would be obliged to take a broader and more comprehensive view of their problem and its purpose than at present. We have discussed the feasibility of this plan with competing interests in a number of cases and have frequently had the proposition pried by the insistence upon the part of some managers that his company would not be interested in a development that it could not monopolize. Coöperation on the part of several and a monopoly of the results by one is an insoluble problem from the standpoint here proposed.

It is not necessary or even desirable that the results of coöperative research be thrown open to pub-

lic use. Such results should be and remain the exclusive property, for a limited period at least, by patent or otherwise, of those who contribute to the development. There is already, especially in this country, too little regard and protection for the rights of pioneers who have spent their money and taken their chances in order to further industrial development. Any scheme which would open greater opportunities to industrial piracy would be disastrous to development, and successful coöperation on specific research problems of common interest would have to carry with it a plan for the protection of the rights of the developers. The right to coöperate in the researches should not be denied to any one to whom the results would be of value, but the opportunity for pirating the results without proper compensation should be denied.

The Sherman law has been cited as a legal obstacle to the development of coöperative research. This law was enacted for the prevention of monopoly in restraint of trade. The prevention of industrial development was certainly not contemplated, and it is doubtful if such a construction could ever be put upon its provision. Well intended laws are sometimes diverted to strange uses and already we are confronted with the distortion of this law in ways calculated to produce political effect. The sundry civil bill passed by the last congress provided \$300,000 for prosecuting combinations under the Sherman law but carried an additional provision, the motive for which can not be misunderstood, that none of the money was to be used in prosecuting combinations of labor or combinations of farmers.

If by any conceivable interpretation or motive the Sherman law should be construed as preventing the coöperation of industrial institutions in the study of scientific and engineering problems of mutual interest, it is our duty to show the malinterpretation of the law and indicate proper amendment. If chemistry is to be regarded as an important profession its organizations must consider affairs affecting its interest and the interests of its industrial constituents. Chemists and engineers have stood until recently, without protest, ridiculous abuses in our patent laws and practices. As soon as they concentrated their efforts on needed reforms the Supreme Court recognized the justice of their protests, recast the rules of practice, and now we are looking forward to a revision of the patent laws which will better protect the interests of the professions concerned.

It has been said that the most important step in invention is to realize a need. If the chemical profession will realize the need of more scientific study of industrial problems and the great possibilities of coöperation in the study of specific problems by interested industrial groups it is our duty to discover the way for the accomplishment of this need.

THE CONTROL OF PUBLIC UTILITIES

Up to the beginning of the legislative sessions of 1913, fourteen states—Wisconsin, New York, Maryland, New Jersey, Vermont, Ohio, Washington,

California, Nevada, Oregon, Kansas, New Hampshire, Connecticut, and Rhode Island—had established commissions for the control of public utilities. Massachusetts divided many of the same powers among three commissions, and several states gave a part of the same powers to other commissions, such as, for example in Oklahoma, to the corporation commissions.

Following considerable agitation, eight states—Indiana, Illinois, Colorado, Missouri, Montana, Idaho, Pennsylvania, and West Virginia—created public utilities commissions during the legislative sessions of 1913. Massachusetts conferred the duties of the highway commission relating to telegraphs and telephones and the duties of the railroad commission upon a new public service commission; Ohio redrafted the public utility commission law, giving additional powers especially relating to valuation and to stock and bond issues; and New Hampshire amended her law by giving the commission power over accounting, including depreciation. In each case the commission is made appointive by the governor.

These laws uniformly require that public utilities shall give just and reasonable service at a just and reasonable rate, and in most states the commissions are given ample power for investigation and enforcement. The municipal utilities placed under control in the different states are mainly heat, light, water and power companies, street railways, and telephone and telegraph companies. In most of the states,

railroads, other common carriers and similar services are also controlled.

Discrimination is prohibited in service and rates; free service to any but certain excepted classes is prohibited, and, in all but West Virginia, issues of stocks and bonds are placed under the regulation of the commission; uniform accounts are provided for, either in a mandatory or optional way, and valuation of the property used and useful for the convenience of the public is authorized in nearly all of the states. In Indiana and Ohio such valuation is required. In almost every state municipally owned utilities are subject to the same regulations as others. The laws make no exceptions for home rule. A strong effort was made in Illinois to except Chicago from the law, but it failed. It may be said in general that the state commission is supreme in most matters over the municipalities, although much power is left to the latter to regulate and control. The cities grant franchises and regulate by contract or otherwise the service and condition of occupying of the streets. In Indiana the indeterminate permit is provided for after the manner of the Wisconsin law.

A consideration of the new public utilities acts shows that there is a tendency to give real powers to the commissions. With the exception of the laws passed in Massachusetts and West Virginia, the acts of the year represent nearly all of the best which have been demonstrated to be empirically good in other states.

W. A. HAMOR

ORIGINAL PAPERS

THE PROTECTION OF IRON AND STEEL BY PAINT FILMS

By NORMAN A. DUBOIS

Received October 4, 1913

The theories of corrosion of iron and steel which have received consideration and which still seem to have their defenders and opposers are interesting to note. The carbonic acid theory in brief requires the presence of carbonic acid to start corrosion. The peroxide theory supposes that hydrogen peroxide is formed in the presence of moisture and oxygen, and that this hydrogen peroxide causes corrosion. The electrolytic theory assumes that iron passes into solution in water in the form of a ferrous ion before it can oxidize. A more or less complete discussion of these theories may be found in the various journals and other publications. It is not the purpose of this paper to discuss them.

From the standpoint of the paint technologist the problem is that of finding the paint film which will enable him to protect the exposed surface of iron and steel from the various rusting influences for the longest possible time. The theories of corrosion and numerous discussions of them have been of inestimable value, and the proper interpretation of them has enabled the paint technologist to improve his paint film. Let us briefly consider these theories from the standpoint in question.

The carbonic acid theory requires the presence of carbonic acid that corrosion may proceed. In other words, considering a paint film properly applied over the surface of iron and steel it requires that carbon dioxide shall pass through this film, and also that water, either as such or in the form of aqueous vapor, shall pass through the film, and there in conjunction with the carbon dioxide react as carbonic acid. The imperviousness of the paint film to carbon dioxide gas and to aqueous vapor, then, is the vital quality from the standpoint of this theory. The more impervious the paint film to the gases carbon dioxide and aqueous vapor, the longer it will protect the iron or steel from corrosion.

The peroxide theory requires the formation of hydrogen peroxide on the surface of the iron or steel. Considering a paint film properly applied over the surface of iron or steel, therefore, this means that the less pervious the paint film is to the gases oxygen and aqueous vapor, the smaller will be the quantity of hydrogen peroxide formed on the surface of the iron or steel, and the longer it will protect the iron or steel from corrosion.

The electrolytic theory requires that iron first pass into solution in water as ferrous ion, and that it is then acted upon by oxygen dissolved in the water or by carbon dioxide and water to form rust. Again considering a paint film properly applied over iron or

steel this theory requires the presence of water in which the iron may dissolve to form ferrous ions. Obviously, the only way the water can get to the iron or steel is to pass through the paint film, as such, or in the form of aqueous vapor. If we suppose the ferrous ions have been formed, the action can go no further in the absence of an oxidizing agent, presumably oxygen, which in turn must get through the paint film. The reasoning for the presence of other gases is similar. We find, therefore, that for corrosion to proceed according to the electrolytic theory the gases, aqueous vapor, oxygen, or others must pass through the paint film, and as in the other cases, the more impervious the paint film to gases and moisture, the longer it will protect the surface of the iron or steel from corrosion.

This is but to conclude that the paint film which will serve for the longest time as a protection to iron or steel against corrosion is the one which is the least pervious to aqueous vapor, the gases oxygen and carbon dioxide, or in fact any gas in the surrounding atmosphere which may in any way cause or accelerate corrosion.

If we assume the corrosion to be entirely due to the deterioration of the paint film rather than to its permeability to aqueous vapor and other gases, the same conclusion holds, as the rate of deterioration will be proportional to the permeability of the film to the deteriorating elements.

The electrolytic theory of corrosion has given rise to a division of pigments into three classes: corrosion accelerators, corrosion inhibitors, and inerts. While these pigments seem to give results as predicted by this theory in the presence of abundance of water or when the iron or steel is actually immersed in water, it does not necessarily follow that they will do so, to a like extent at least, when incorporated in a paint film where conditions are much different.

Assume, for instance, that our paint film is somewhat pervious to aqueous vapor and other gases. It follows that just as moisture may enter to the iron or steel surface and perhaps give conditions under which the electrolytic theory may apply when outside conditions are damp, this moisture may also pass from the steel surface outward when outside conditions are dry, and thus leave the steel surface dry in which case the electrolytic theory cannot possibly apply. As a matter of fact, the actual conditions existing on the surface beneath the paint film, in most instances, are very probably between the two extremes of somewhat damp and nearly dry, and this is far from being covered with an abundance of water at all times, the conditions under which the electrolytic theory seems to work out well. This reasoning is borne out by the fact that a piece of bright steel immersed in water containing a little zinc chromate in suspension will remain bright perhaps indefinitely, while the same pigment in a paint film under ordinary conditions will not protect the steel in a like manner.

Again, two paints composed of the same vehicle, but the first containing a so-called corrosion accelerator only, painted on a steel surface in a locality of ordinary dryness will outlast to a great extent the second containing a rust inhibitive pigment painted on a

steel surface in a locality habitually very damp.

This reasoning seems to indicate and the evidence seems to bear out the conclusion that the problem of iron and steel preservation is rather to be solved by making our paint film as nearly impervious to gases as possible, than by trying to prevent corrosion by the addition of the so-called inhibitive pigments.

The problem is a physical one rather than a chemical one, and a comparison of paint films as to their relative obstruction to the diffusion of gases will tell more regarding their value as protection against corrosion than a study of the inhibitive action of their pigments. This is not to say that the inhibitive property of certain pigments is not worth consideration, but the imperviousness of the films is of far greater importance.

The work to be described here was carried out for the purpose of determining whether a special formula paint made according to the foregoing principles, embodying diffusion retarders, would not outlast in protecting qualities those made according to the formulas accepted as first quality paints for their respective purposes.

Our prime object is to make the film as impervious to gases as possible. This may be accomplished to a certain extent by special treatment of the vehicle and by incorporating special pigments and pigment combinations. It is well known that a film from the oxidation of pure linseed oil, *i. e.*, a film of linolein, is more or less permeable to moisture and gases. It is more or less porous. If other oils or gums, or similar materials, can be incorporated with the linseed oil to form a homogeneous mass which as a whole acts as a perfect vehicle as regards compatibility of properties, it is readily understandable that such treatment may, to an extent, fill the intermolecular spaces between the linseed oil molecules, just as in other cases of solution, alloy, or mixture; and this compound vehicle will be more dense, will leave a film which offers more resistance to the diffusion of gases, and will, therefore, protect the iron and steel for a longer time (assuming other things equal) than a film which has not been treated in this way.

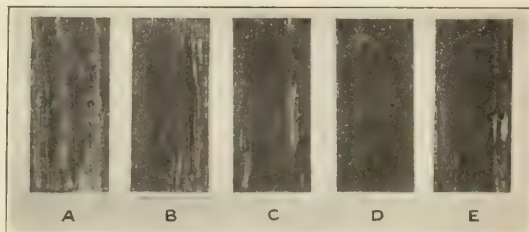


PLATE I—STEEL PANELS PAINTED WITH PAINTS OF SAME FORMULA EXCEPT ONE CONSTITUENT OF THE VEHICLE

Plate I shows five steel panels which, after thorough cleaning with hot 10 per cent solution of sulfuric acid for twenty minutes, washing by immersion in dilute caustic solution, thoroughly washing with water, and quickly drying, were painted as follows. All paints were of the same formula, with the exception of one constituent in the vehicle.

Panel A is a pure linseed oil vehicle.

Panel B contains 5 per cent of Kauri mixing varnish in the vehicle.

Panel C contains 10 per cent of Kauri mixing varnish in the vehicle.

Panel D contains 20 per cent of Kauri mixing varnish in the vehicle.

Panel E contains 30 per cent of Kauri mixing varnish in the vehicle.

These were exposed in a closed box with a glass front, in order that the conditions could be carefully watched. Oxygen and the corrosion accelerating gases in the atmosphere were passed into the box through wash bottles, to insure a slow but steady current, and a small quantity of steam was admitted to keep the atmosphere within the box always very moist, but not sufficient to raise the temperature materially. The panels were examined from day to day, and removed when it was judged that further exposure might obliterate the truths for which we were seeking.

It is very evident that the panels at both ends have failed before those between. A relation may also be seen between the duration of protection and the quantity of Kauri mixing varnish in the vehicle. The protecting qualities increase with the per cent of Kauri mixing varnish to a certain point, and then fall off again as the percentage of Kauri mixing varnish is increased beyond this point. This seems to indicate a definite point of maximum sealing effect for this particular material.

Another illustration of making a paint less pervious and therefore a better protection against corrosion, is the proper choice of pigments. Red lead and linseed oil have been long looked upon as the best primer for iron and steel. This may be true, but is it not possible to improve this red lead and linseed oil without seriously changing its nature and obtain a film which is less pervious to gases and moisture and thereby protect the iron and steel even more effectively than

alum voids, to produce a red lead primer, which has all the advantages of the traditional red lead and linseed oil, and is at the same time less pervious, and therefore a better protection against corrosion.

Plate II shows a series of pairs of steel panels, which have been cleaned in the usual manner with acid, etc. Both A and B of each pair were painted with the same second coat paint, and each pair with a different second coat paint, while A of each pair was primed with a special red lead paint, formulated according to the principles just mentioned, and B of each pair was primed with red lead and linseed oil mixed according to a formula considered to give the best results obtainable after many years of practical painting under more or less adverse conditions of moisture and corrosion accelerating gases. All the panels were painted in exactly the same manner on the same

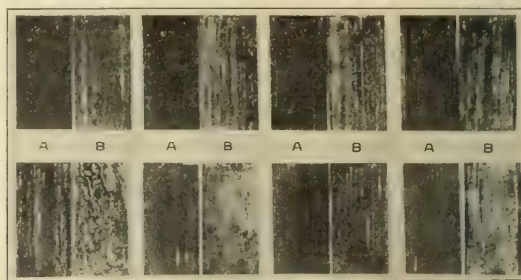


PLATE III—PAIRS OF STEEL PANELS PAINTED WITH SO-CALLED RUST PROOF PAINTS

A's primed with special red lead paint
B's primed with rust proof paint
All second coats of rust proof paint

day, allowed the same time to dry between coats and also after the second coat, and exposed as previously described at the same time and for the same length of time. Since the second coat on A and B is the same in each instance its effect has nothing whatever to do with the comparison, this being dependent entirely on the difference in the red lead priming paints on A and B. It can be seen at a glance that the special red lead paint on A has given a much more efficient protection than that mixed according to the prevailing custom on B. One hundred and twenty comparison panels were exposed in this test and in every instance panel A showed a better film than did panel B.

Lastly, let us take up for a brief space the incoming of the throng of fantastically named "paints" which have been put on the market with claims equally as fantastic. Many of these have been claimed to protect the iron and steel as a primer and as a second coat better than anything on the market. It is only necessary to refer to Plate III, which is a photograph of some pairs of steel panels prepared as before mentioned and painted with a number of so-called rust inhibitive or rust proof paints. On panels marked B was painted two coats of a paint, and on panels marked A one coat of the same paint over a priming coat of the special red lead paint formerly mentioned. As a different paint is on each pair there are as

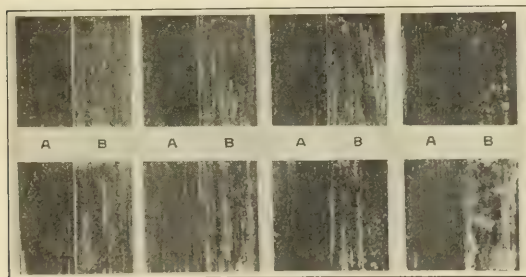


PLATE II—PAIRS OF STEEL PANELS
A's primed with special red lead paint
B's primed with usual red lead paint
All painted with same second coat paint.

will the red lead and linseed oil? If we shake off some of the traditional bonds and apply the teachings of more recent scientific investigation we find it possible by using the foregoing principles and the proper choice of particle sizes, making use of the law of mini-

many different paints as there are pairs of panels.

It is readily seen that the two coats of any of these paints, B, do not protect as well as where it is applied over the special red lead primer, A.

Blue lead seems to have certain properties very similar to red lead when used in a paint for the priming of iron or steel, and in fact it is very possible that it may be fully as good for this purpose as red lead, when properly used, if not better. Experiments are now being conducted by the writer to determine these relations.

Recently the idea has been set forth that certain pigments are rust inhibitive by virtue of their alkaline qualities. Further investigation seems necessary to determine whether it is simply the alkaline properties of these pigments considered as a rust inhibitive only which endows the paint film with superior protecting qualities.

The suggestion may not be out of place that the basic properties of certain pigments enable them to attack the vehicle to a sufficient extent to form a small quantity of metallic soap which acts as a binding material between the pigment particle and the linolin, thus offering a greater obstruction to the passage of disintegrating elements between pigment particle and vehicle; or perhaps acting as a diffusion retarder in the linolin.

It is not the intention of the writer to point out the shortcomings of any particular brand of paint or theory, but simply to give results of experiment and interpretation of the same with a view to bettering the paint conditions for all concerned.

In conclusion then, it would seem that whatever the correct theory of corrosion may be, it is of first importance to the paint technologist to construct his film in such a manner as to exclude gases and moisture to the greatest possible extent, as without these no corrosion can possibly take place.

LABORATORIES OF THE GORDON-HITTL CO.
BOSTON

THE OLEORESINS OF JEFFREY AND SINGLELEAF PINES

By A. W. SCHORGER

Received September 25, 1913

The Forest Service for a number of years has been investigating the possibilities of utilizing various species of conifers for the production of naval stores. The following work on Jeffrey and singleleaf pines is a continuation of the examination of the oleoresins obtained during the tapping experiments. The methods of analysis employed and the results obtained in the examination of other species will be found in another publication.¹

The oleoresins of the pinon pine¹ (*Pinus edulis*, Engelm) and singleleaf pine (*Pinus monophylla*, Torr, and Frem.) are similar in composition, appearance, and odor. Both oleoresins contain large resin acid crystals and have a pungent characteristic odor. The volatile oils of the two species consist mainly of α -pinene and the sesquiterpene cadinene is found in the higher boiling portions. In addition, β -pinene

and probably limonene¹ occur in the oil from *Pinus edulis* while limonene occurs in the oil of *Pinus monophylla*.

Attention has been previously² called to the confusion caused by lack of an exact knowledge of the species yielding heptane. The source of this substance has been variously ascribed to one or more of the following species: Western yellow pine (*P. ponderosa*, Laws); digger pine (*P. sabiniana*, Dougl.); and Jeffrey pine (*P. jeffreyi*). It has been previously² shown that the oil from *Pinus ponderosa* does not contain heptane and that the oil of *Pinus sabiniana* consists of nearly pure heptane. It is now possible to confirm the work of Blasdale³ and Wenzell⁴ since examination of authentic samples of the oleoresin of *Pinus jeffreyi* has shown that the oil consists largely of normal heptane.

The lack of uniform data in the literature regarding the resin acids is much to be regretted. The melting point of abietic acid from colophony varies from 135°⁵ to 165°.⁶ Tschirch⁷ states that American colophony contains α -, β -, and γ -abietic acids melting at 155°, 158°, and 153-154°, respectively, and then obtains abietic acid, melting point 166-167°, from rosin oil.⁸

Leuchtenberger,⁹ working under Tschirch, examined the colophony of *Pinus jeffreyi*. Extraction of an ether solution of the colophony with one per cent (NH₄)₂CO₃ gave four per cent of α -Jeffropinic acid, C₁₀H₁₄O₂, m. p. 160-161°; nine per cent β -Jeffropinic acid, C₁₂H₁₈O₂, m. p. 81-82°. Extraction with one per cent Na₂CO₃ solution gave 35 per cent α -Jeffropinolic acid, C₁₄H₂₀O₂, or C₁₄H₂₂O₂, m. p. 117-118°; 38.2 per cent β -Jeffropinolic acid, C₁₄H₂₀O₂, or C₁₄H₂₂O₂, m. p. 77-78°. The acid isolated by the author from the oleoresin of *P. jeffreyi* melted at 170-171°. The silver salt contained 26.16 per cent of Ag, agreeing with the formula C₂₀H₃₀O₂. The acid from the colophony melted at 137-8° crystallized from acetone and 145-6° crystallized from acetone and hydrochloric acid. α -Jeffropinic acid requires 39.51 per cent Ag and α -Jeffropinolic acid, C₁₄H₂₀O₂, requires 32.98 per cent Ag. To obtain acids of this formula it would be necessary for the resin crystals existing in the oleoresin to undergo profound alteration in heating to 145° C. which is not borne out by experience. The action of acids and alkalis has a material effect on the melting point of the resin acid. Valente¹⁰ obtained an acid from French colophony melting in the crude state at about 160°. When purified by solution in dilute sodium carbonate and precipitation with dilute sulfuric acid, the resin acid melted at only 146-148°.

EXPERIMENTAL

Oleoresin of *Pinus monophylla*

Oleoresin.—Analysis of the crude oleoresin gave

¹ Loc. cit., 29.

² "An Examination of the Oleoresins of Some Western Pines," by A. W. Schorger, Forest Service, Bull. 119.

³ Blasdale, *J. Am. Chem. Soc.*, **23**, 162-4 (1901).

⁴ Wenzell, *Pharm. Rev.*, **22**, 408-14 (1904).

⁵ Flückiger, *J. prakt. Chem.*, **101**, 235 (1867).

⁶ Maly, *Sitzungsber. d. k. Akad. d. Wis. zu Wien*, **44**, 121 (1861).

⁷ "Die Harze und die Harzebehälter," 2nd ed., 1906, p. 660.

⁸ *Arch. Pharm.*, **245**, 1 (1907).

⁹ *Ibid.*, **245**, 701-7 (1907).

¹⁰ *Atti della R. Accad. dei Lincei*, **1**, [4] 13 (1884).

¹ "An Examination of the Oleoresins of Some Western Pines," by A. W. Schorger, Forest Service, Bull. 119.

the following percentages: Volatile oil 10.00 per cent; colophony (grade N) 70.63 per cent; trash, needles, bark, etc., 0.11 per cent; water 1.26 per cent.

Volatile oil.—The properties of the oil were as follows: d_{15}^0 0.8721–0.8733; n_D^{15} 1.4732–1.4733; α_D^{20} +14.41° to +17.26°. Five hundred grams of the oil gave the following results on fractionation:

Temp. (corr.) ° C.	Distillate observed Per cent	Distillate cumulative Per cent	d_{15}^0	n_D^{15}
155.9–156.9	4.75	4.75	0.8602	1.4674
157.0	10.25	15.00	0.8603	1.4676
157.1	10.25	25.25	0.8602	1.4677
157.2	10.20	35.45	0.8599	1.4678
157.4	10.33	45.78	0.8598	1.4679
157.8	9.94	55.72	0.8594	1.4680
158.2	9.80	65.52	0.8588	1.4680
160.0	10.52	76.04	0.8576	1.4685
171.8	10.07	86.11	0.8536	1.4705
190.0	3.99	90.10	0.8511	1.4818
	9.80	99.90		

α -Pinene.—After repeated fractionation 398.5 grams of oil were obtained boiling below 160°. Ten grams of a fraction, b. p. 155.5–157°, d_{15}^0 0.8612, α_D^{20} +35.36°, gave only 0.78 gram (7.8 per cent) of pinene nitroschloride, m. p. 99°; nitrolpiperidine, m. p. 118°. The low yield of nitroschloride is doubtless due to the high optical rotation of the pinene fraction. The fraction, b. p. 160–170°, weighing 21.5 grams was examined for β -pinene with negative results.

Limonene.—The limonene fraction weighing 17.5 grams had the following properties: b. p. 170–180°; α_D^{18} —1.18°. A crystalline tetrabromide was not obtained but a dihydrochloride, m. p. 49°, was easily secured.

Cadinene.—The residue remaining from the original fractionation was distilled from a Ladenburg flask and two fractions collected: (1) b. p. 200–250°, 18.5 grams; (2) b. p. 250–280°, 20.2 grams; α_D^{25} +10.58°. Fraction (2) was found to contain cadinene as shown by a dihydrochloride, m. p. 117–118°. A 6.14 per cent ethereal solution gave α_D^{35} —2.02°. In the examination of *d*- and *l*-cadinene from various oils the rotation of the cadinene dihydrochloride has always been found to be negative.

Colophony.—The colophony had the following constants: Acid no. 155.9 by direct titration; sap. no. 163.3. When the colophony was treated with an excess of *N*/2 alcoholic potash it yielded 7.22 per cent of resene soluble in petroleum ether. The colophony on being dissolved in acetone and allowed to stand in an ice box for a month deposited a mass of resin crystals. These crystals were mechanically freed from oily impurities so far as possible, rapidly stirred in cold acetone and the solvent decanted. After four crystallizations from the same solvent, the crystals obtained melted at 119–120°, and were completely liquid at 129°. The resin crystals contained in the original oleoresin were freed from the greater portion of the adherent oil by suction. The resulting white, waxy cake was recrystallized six times from acetone. The crystals obtained melted at 129–130° and were completely liquid at 135°. Analysis of the silver salt of the acid follows:

0.2214 gram of silver salt gave 0.0590 gram Ag = 26.65 per cent.

Silver abietate, $Ag(C_{20}H_{29}O_2)$, requires 26.37 per cent Ag.

Oleoresin of *Pinus jeffreyi*

Oleoresin.—The analyses contained in the following table are of interest in that they represent samples from individual trees.

No.	Volatile oil Per cent	Water Per cent	Trash Per cent	Colophony Per cent	Volatile oil	
					d_{15}^0	n_D^{15}
1	11.25	1.23	0.46	87.06	0.7013	1.3963
2	8.81	1.50	0.44	89.25	0.7018	1.3958
3	9.73	2.29	0.23	87.75	0.6951	1.3927
4	10.96	1.42	0.80	86.82	0.7110	1.4002
5	9.05	2.00	0.40	88.55	0.7008	1.4060
Mean	9.96	1.69	0.47	87.88		

Volatile Oil.—The properties of the volatile oils are given in the preceding table. The oils from the five samples were mixed and 175 grams distilled from a Ladenburg flask with the following results:

Temp. (corr.) ° C.	Distillate observed Per cent	Distillate cumulative Per cent	d_{15}^0	n_D^{15}
98.2–98.8	16.74	16.74	0.6880	1.3902
100.0	40.47	57.21	0.6889	1.3903
102.0	22.92	80.13	0.6897	1.3905
105.0	8.17	88.40	0.6906	1.3915
113.0	4.05	92.45	0.6965	1.3937
...	7.37	99.82

Heptane.—The first four fractions amounting to 150 grams were redistilled, using a 12-inch Hempel column with the following results:

No.	Temp. (corr.) ° C.	Distillate observed Per cent	Distillate cumulative Per cent	d_{15}^0
1	98.1–98.3	19.20	19.20	0.6878
2	98.4	40.95	60.15	0.6881
3	98.5	30.07	90.22	0.6881

The boiling points and specific gravities of the fractions are practically identical with the constants of pure *n*-heptane.

Citronellal.—The residue boiling above 113° distilled mainly between 200–215° C. The fraction with the latter boiling point weighed 6 grams (3.4 per cent) and had: d_{15}^0 0.8578; n_D^{20} 1.4570; α_D^{20} —2.50°. The oil had a lemon odor and showed the following properties of an aldehyde: Combined with $NaHSO_3$ forming a flocculent precipitate, reduced an ammoniacal silver solution, and produced a rose-red coloration with a fuchsin solution decolorized with SO_2 . The semicarbazone obtained separated as oil that crystallized after standing in the cold for several days. The semicarbazone was twice recrystallized from alcohol, finally from a mixture of chloroform and petroleum ether. The crystalline powder obtained melted at 91–92°. Lack of material prevented the satisfactory formation of other derivatives. Comparison with the properties of citronellal from Java lemon oil¹ follows:

Source	B. p.	d_{15}^0	n_D^{20}	Optical rotation
Java lemon oil	205–208°	0.8567	1.44791	α_D —3°
<i>Pinus jeffreyi</i>	200–215°	0.8578	1.4570	α_D^{20} —2.50°

¹ Schimmel and Company, *Berichte*, April, 1903, p. 21

Active citronellalsemicarbazone, $C_{10}H_{18} : NNHCONH_2$, melts at 82.5° , the racemic form at 96° . From the optical rotation of the aldehyde fraction of *Pinus jeffreyi* it is possible that the semicarbazone contained a small amount of the active form resulting in the low melting point obtained.

Colophony.—A sample of "ww" colophony had the following properties: Acid no. 147.6; sapon. no. 178.1. The rosin contained 12.5 per cent of resene obtained in the form of a yellow, very sticky, viscous syrup. The colophony crystallized from acetone after standing in the cold for several weeks, differing in this respect from the colophony of *Pinus sabiniana*. The crystals obtained after five recrystallizations from acetone softened at 130° and melted at $137-8^\circ$. When followed by a crystallization from a mixture of acetone and hydrochloric acid they softened at 136° and melted at $145-6^\circ$, becoming completely liquid at 151° .

The resin crystals obtained from the crude oleoresin melted at $170-171^\circ$. The silver salt of the acid was prepared and analyzed as follows:

0.3926 gram of silver salt gave 0.1027 gram Ag = 26.16 per cent Ag.

Silver abietate, $Ag(C_{20}H_{25}O_2)$, requires 26.37 per cent Ag.

SUMMARY

The volatile oil of *Pinus monophylla* contains 80-85 per cent *d*- α -pinene; 4-5 per cent *l*- or *i*-limonene; 4-6 per cent *d*-cadinene; losses by polymerization, etc., 4.5 per cent. The colophony contains 7.22 per cent resene and resin acids isomeric with abietic acid.

The volatile oil of *Pinus jeffreyi* contains about 95 per cent *n*-heptane and 5 per cent of an aldehyde, apparently citronellal. The colophony contains 12.5 per cent resene and resin acids isomeric with abietic acid.

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

THE HYDROCARBONS OF UTAH¹

By CARLOS BARDWELL, B. ARTHUR BERRYMAN, THOMAS B. BRIGHTON
AND KENNETH D. KUHR

Received September 20, 1913

About fifteen kinds of hydrocarbons occur in Utah; the five of these occurring most abundantly—gilsonite, tabbyite, wurtzilite, ozocerite and rock asphalt—are the ones selected for this investigation.

Gilsonite² (uintaite) was first described by Blake in 1885. He gave it the name uintaite because of its occurrence in the Uinta Mountains. Later the name gilsonite was adopted because S. H. Gilson, a prospector, brought it into prominence as an article of commerce. The deposits of gilsonite are limited to the Uncompahgre Indian Reservation in Uinta County, being found in an area extending along the 40th parallel for about 60 miles.

Tabbyite receives its name from an Indian chieftain, Tabby. The deposits are in Tabby Canyon, a branch of the Duchesne, about 8 to 9 miles south and west of Theodore, Uinta County.

¹ This work was done at the suggestion and under the direction of Dr. W. C. Ebaugh, to whom the authors' thanks are due.

² Blake, *Eng. Min. J.*, **40**, 431 (1885).

Wurtzilite³ (elaterite or mineral rubber) from Utah was first described by Wurtz, who showed that it is a distinct mineral. The name elaterite had been used previously by Dana and other mineralogists to describe three different minerals of specific gravities ranging from 0.905 to 1.223. The region in which wurtzilite is found covers an area of about 100 square miles between Indian Canyon and Sam's Canyon, branches of Strawberry Creek, about 30 miles due north of Price, Utah.

Ozocerite (mineral wax) has been known for many years on account of the economic value of the large deposits in Galicia, Austria. The only other deposit known to be of commercial value is that in Utah. This deposit begins about two miles west of Colton, Utah County, and extends to about four miles west of Soldier Summit, a distance of 12 miles. The belt is 2 miles wide. This area may be divided into three parts:² (1) near Colton, on the north side of the Price River valley; (2) to the east of Soldier Summit where the railroad crosses the crest of the plateau; and (3) near Midway Station, on the north side of the canyon, near the source of Soldier's Creek.

Heretofore rock asphalt has usually been called bituminous sandstone, but the former name is growing in popularity, especially in Utah. The largest deposit in the state lies south and east of Vernal, north of the White River and between Ashley and Uinta valleys.³ This deposit attains a thickness (in places) of twenty feet, but at present it is too far from a railroad for successful commercial exploitation. Another deposit occurs in Spanish Fork Canyon, southeast of Thistle, and still other immense deposits are found (1) in the tributaries of Whitmore Canyon, near Sunnyside, (2) at the head of Willow Creek, a tributary of the Green River, in the Book Cliff Mountains, and (3) in the Laramie sandstones near Jensen, on the Green River. A deposit of bituminous limestone occurs at the head of the right-hand branch of Tie Fork, a canyon entering Spanish Fork Canyon, 2 miles west of Clear Creek Station. An area underlaid by bituminous limestone, about 50 miles long east and west by 10 miles wide north and south, lies just north of Colton and south of Strawberry Creek, extending from Antelope Creek on the east to Thistle on the west.⁴

HISTORICAL

In reviewing the literature of these substances one finds that a great deal has been published concerning gilsonite and ozocerite, but not much about wurtzilite, tabbyite and rock asphalt. Day,⁵ working with gilsonite, attempted to isolate "such single hydrocarbons or their derivatives as would give some information as to the real nature of the mineral itself." He gives an outline of the physical characteristics, solubilities, etc., of gilsonite, and describes the character of the residue from each solvent as well as the nature of the dissolved portion. Proximate and ultimate analyses

³ Wurtz, *Ibid.*, **49**, 59 (1890).

² Taff and Smith, U. S. Geol. Survey, Bull. **285**, 369 (1905).

³ Wigglesworth, *Trans. Am. Inst. Min. Eng.*, **17**, 115 (1888).

⁴ Eldridge, U. S. Geol. Survey, 17th Ann. Rept., **1896**, 915, et seq.; 22nd Ann. Rept., **1900-01**, 332.

⁵ Day, *J. Frank. Inst.*, Sept., **1895**, 221, et seq.

are given. From a study of the distillation products of gilsonite he concludes that the oil obtained belongs to the paraffin series of hydrocarbons, and is made up of a number of distinct substances, just as is petroleum. He obtained from the distillate volatile with steam, oils which seem to correspond to those described by Peckham¹ as obtained from California bitumens. These had an odor similar to quinoline, and to him this was an evidence of the relationship of California bitumen and of gilsonite and of their animal origin. Day gives also the results of treatment with nitric acid and descriptions of the products and their properties, concluding that some members of the naphthalene series are present.

Eldridge² described the location of the hydrocarbon deposits and the geology of the district. He states that the cracks in which gilsonite is found were formed by the gentle folding that produced the Uinta Valley syncline. He describes the properties of the gilsonite coming from near the surface where, through atmospheric agencies, it has lost its luster and become pencilled in structure. From a study of conditions he concludes that the gilsonite found its way into the fissures as a plastic mass, coming from below under pressure, and though of high viscosity, sufficiently fluid to be pressed between the grains constituting the wall rocks. He frankly confesses his lack of ability to suggest the condition under which the gilsonite existed prior to its flow into the cracks. An analysis of gilsonite by Day is quoted as follows:

	Percentages
Volatile matter.....	56.46
Fixed carbon.....	43.43
Ash.....	0.10
or	
Carbon.....	88.30
Hydrogen.....	9.96
Sulfur.....	1.32
Ash.....	0.10
Oxygen and nitrogen (undetermined).....	0.32

Locke,³ Blake,⁴ Raymond,⁵ and Wurtz⁶ describe the uses of gilsonite, its solubilities, methods for "fluxing" it, etc. The earlier analyses of asphalts gave rather large percentages of oxygen, but this was probably because the presence of sulfur had not been recognized and the oxygen was supposed, with the carbon and the hydrogen, to make up the ash-free bitumen. Nevertheless some analyses which report sulfur and nitrogen also report small amounts of oxygen.⁷ By some authorities, as Richardson and Peckham, oxygen is considered as foreign to natural asphalts.

In the first reference to wurtzilite, Blake⁸ describes it from a physical standpoint, noting its occurrence, hardness, color, specific gravity, fusibility, electrical properties, etc. He explains the difference between wurtzilite and gilsonite,⁹ and shows that the Utah wurtzilite is an entirely distinct mineral from the elater-

ite of Dana and other mineralogists. Wurtz¹ confirms the conclusions of Blake.

Utah ozocerite is very similar in properties to that from Galicia, but as it contains less oily material and is firmer, it is more valuable. Many popular accounts² of its mode of preparation, uses, etc., are to be found, but nothing concerning its chemical composition, distillation products, etc.

With the exception of occasional references to the location of bituminous sandstones in Utah, nothing could be found about rock asphalt.

USES OF UTAH HYDROCARBONS

An investigation of the uses of Utah hydrocarbons shows them to be surprisingly numerous and varied. Many of our commonest articles are made from these substances. Before the discovery of gilsonite in Utah, European and Asiatic asphalts were shipped into the United States; now, because of its abundance and purity large quantities of Utah asphalt are shipped to foreign countries. The production of gilsonite during the last two years has increased rapidly, due to the greater number of articles made from it. In 1910³ the production was 30,000 tons; in 1912, over 50,000 tons. It is worth about \$20.00 a ton, f. o. b. Utah.

Wurtzilite is little used because of its insolubility. About 1,000 tons are produced annually.

Ozocerite is of greater value than gilsonite, the price in New York being 15 to 28 cents per pound.⁴ No data could be found as to the production of ozocerite, but at present the demand far exceeds the supply.

Perhaps the most extended use that has been made of Utah asphalts is in the paving industry. Gilsonite has been used in paving the streets of many important cities,³ e. g., Michigan Avenue, Chicago, where it is said to be giving satisfaction under the most exacting requirements. Rock asphalt was used³ in paving Second South Street between West Temple and First West Streets, Salt Lake City, and the surface is now in fair condition, although it has had practically no repairs during its 16 years of service.

Another important use for Utah hydrocarbons is in the manufacture of varnishes and paints.³ Only the purest and best materials are used for these purposes, the refined hydrocarbons being dissolved in turpentine and linseed oils. Wurtzilite has been used in the manufacture of a varnish in which the particles are simply held in suspension, but do not enter into solution.

Some of the uses of the individual Utah hydrocarbons are as follows:

Gilsonite.^{3,5}—Paving industry, electrical insulators, roofing papers and compounds, water-proofing wooden and steel pipes and masonry aqueducts, preventing electrolytic action on iron plates of ship bottoms,

¹ Wurtz, *Eng. Min. J.*, **49**, 106 (1890).

² Higgins, *Salt Lake Mining Review*, **14**, 11-5 (Oct., 1912). Culmer, *Salt Lake Tribune* (Dec. 29, 1912); Taff and Smith, U. S. Geol. Survey, *Bull.* **285**, 369 (1905).

³ Culmer, Address, Univ. of Utah, Nov. 15, 1912.

⁴ Higgins, *Salt Lake Min. Rev.*, **14**, 11-5 (Oct. 15, 1912).

⁵ Locke, *Trans. Am. Inst. Min. Eng.*, **16**, 162 (1887); New Internatl. Encyc. Article on "Asphalt"; Culmer, *loc. cit.*; Richardson and Parker, U. S. Geol. Survey, *Min. Resources of U. S.*, **1893**, 627-69; Taff and Smith, U. S. Geol. Survey, *Bull.* **285**, 369 (1905).

¹ Peckham, *Am. J. Sci.*, **48**, III, 250.

² Eldridge, U. S. Geol. Survey, *22nd Ann. Rept.*, **1900-01**, 330.

³ Locke, *Trans. Am. Inst. Min. Eng.*, **16**, 162 (1887).

⁴ Blake, *Eng. Min. J.*, **40**, 431 (1885).

⁵ Raymond, *Trans. Am. Inst. Min. Eng.*, **17**, 113 (1888).

⁶ Wurtz, *Eng. Min. J.*, **48**, 114 (1889).

⁷ Sadtler, *This Journal*, **5**, 393 (1913).

⁸ Blake, *Eng. Min. J.*, **48**, 542 (1889).

⁹ Blake, *Trans. Am. Inst. Min. Eng.*, **18**, 497 (1889).

coating barb wire fencing, coating sea walls of brick or masonry, lining tanks for chemicals, coating poles, posts and ties, torredo-proof pile coating, smokestack paint, lubricant for heavy machinery, substitute for rubber, as binder pitch for culm in making briquettes and egette coal.

Tabbyite.—Compounds with Para rubber to manufacture floor mats, rubber paints and roofings; as a filler for rubber in automobile tires, etc.

Wurtzite.—Varnishes, roofing compound, etc.

Ozocerite.—Electrical insulator (said to have about four times the specific resistance of paraffin), altar candles, substitute for beeswax, ointments, pomades, salves, water-proofing, waxed paper, wax dolls and figures, telephone receivers, phonograph records, electroplating, water-proof crayons, shoe polish, buttons, cersine, floor polishes and waxes, water-proofing cartridges, sealing wax, etc.

Rock Asphalt.—Paving industry.

EXPERIMENTAL RESULTS

The results of the first tests made upon eight samples of hydrocarbons are given in Table I.² They are

TABLE I

Original substance	Trin.	Ber.	Gils.	Tab.	Wur. 1	Wur. 2	Ozok.	R. A.
Loss 212° F., 1 hr., per cent.....	0.073	0.1765	0.353	0.91	0.53	0.21	0	0.14
Loss 325° F., 7 hrs., per cent.....	1.717	6.63	0.217	2.78	2.76	1.66	45.41	1.43
Penetration residue.....	0	30	0	0	0	0	15	0
New sample loss 400°, 7 hrs.....	5.25	9.71	0.85	6.40	3.88	1.88	65.20	1.79
Penetration residue.....	0	0	0	0	0	0	0	0
Bitumen sol. in CS ₂	60.36	90.93	99.64	94.63	10.83	8.10	99.46	11.34
Org. matter insol. in CS ₂	3.94	3.74	0	0.72	87.68	88.54	0.50	0
Inorg. or mineral matter.....	35.70	5.32	0.36	4.65	1.50	3.36	0.046	88.66
					wt. increased			
Bit. sol. in 62° naphtha.....	41.00	34.40	61.70	58.50	2.76?	2.74?	81.71	9.25
This is per cent of total bit.....	68.00	38.85	61.85	61.85	39.10	33.85	82.20	81.50
Carbenes: bit. insol. in CCl ₄	could not filter	0	0.18	1.75	1.57	1.65	2.51	1.59
Bit. more sol. in CCl ₄	1.37	0	0	0	0	0	0
Original loss on ignition.....	64.30	94.68	99.64	95.35	98.50	96.64	99.96	11.34
Fixed carbon.....	36.69	39.60	43.13	37.45	35.60	10.03	6.85
Sulfur on original.....	4.22	4.70	0.52	1.24	4.00	4.34	0.29	0.78
Specific gravity 78° F.....	1.372	1.05	1.018	1.006	1.032	1.004	0.891	2.097
Streak.....	dark brown	nearly black	brown	brown	brown	brown	brown	brown
Luster.....	dull	glossy	glossy	slightly glossy	glossy	glossy	dull	dull
Fracture.....	conchoidal	conch.	conch.	conch.	conch.	conch.	conch.
Hardness.....	1	<1	2	<1	1	1	<1
Odor.....	tarry	tarry	slightly tarry	petroleum	tarry	tarry	petroleum	slightly oily
Softens ° F.....	203	132	320	264	{ above b. p. }		134
Flows ° F.....	266	181	377	275	{ mercury }		140
Penetration at 78° F.....	0	30	0	0	0	0	30	0

the standard tests recommended by Richardson³ and are meant primarily to determine the fitness of the materials for asphalt paving. No one of the materials as it occurs in nature comes up to the standards completely, but in the cases of Trinidad, Bermudez, rock asphalt and gilsonite the bitumen could be mixed with heavy petroleum oils and given the required penetration and other physical properties. As our work is concerned with the properties of the materials as they occur in nature no compounding was done. For the use of a standard machine for making the penetration tests we are indebted to the office of the City Engineer, Salt Lake City.

The bitumens in asphalts are divided into two general

¹ New Internat. Encey., Article on "Asphalt," Higgins, *Salt Lake Min. Rev.*, **14**, 11-5 (Oct. 15, 1912).

² For purposes of comparison determinations were carried out also upon samples of refined Trinidad and Bermudez asphalt kindly supplied by the New York Testing Laboratory.

³ Richardson, *The Modern Asphalt Pavement*, 1905, 168.

classes,¹ viz., those soluble in 62° naphtha (malthenes) and those insoluble in carbon tetrachloride but soluble in carbon disulfide (carbenes). Our solubility tests were made by allowing one-gram samples, finely ground, to be in contact with excessive amounts of the solvents for 12 to 18 hours, filtering upon ignited asbestos in a Gooch crucible, washing with the pure solvent, drying at 100° C. and reweighing. Great difficulty was found in filtering some of the samples, especially the Trinidad asphalt.

Table II gives the ultimate composition of the samples

TABLE II

Substance	Trin.	Ber.	Gils.	Tab.	Wur. 1	Wur. 2	Ozok.	R. A.
Carbon.....	51.06	77.52	85.25	81.32	76.90	79.40	85.35	9.55
Hydrogen.....	5.84	8.90	10.55	10.40	11.20	10.55	13.86	1.10
Sulfur.....	4.22	4.70	0.52	1.24	4.00	4.34	0.29	0.78
Nitrogen.....	0.66	0.89	2.21	2.10	2.18	2.10	0.36	0.31
Ash.....	35.70	5.32	0.89	4.65	1.50	3.36	0.04	88.05

as determined by the ordinary combustion method, with lead chromate and copper oxide in the combustion tube. Great care must be taken in starting a combustion to prevent the too rapid distillation of the volatile components present in the samples. Nitrogen was

determined by a modified Kjeldahl method, with subsequent distillation into an excess of standard sulfuric acid. Sulfur was determined by a modification of the Eschka method,² i. e., roasting a weighed sample of material with zinc oxide and sodium carbonate, leaching with water, filtering, acidulating with hydrochloric acid, and precipitating and weighing barium sulfate as usual. Ash was determined by (1) reweighing the boat after a combustion, or (2) by burning a one-gram sample in a platinum dish. In two cases the ash was analyzed. The results are given in Table IIa.

TABLE IIa

Ash analysis	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO
Rock asphalt.....	78.20	2.20	9.00	5.60	2.10
Tabbyite.....	35.35	2.50	9.80	29.50	9.45

Table III records the results of a series of solubility

¹ Richardson, *loc. cit.*

² Elbaugh and Sprague, *Jour. Am. Chem. Soc.*, **29**, 1475 (1907).

tests. The treatment with solvent lasted for 18 hours, and a motor-driven shaking device produced thorough mixture of sample and solvent. The hot extractions were made with boiling solvent in a flask fitted with a reflux condenser.

TABLE III

Solvent	Trin	Ber	Gils	Tab	Wur	I	Ozok	R. A.
Amyl alcohol	Insol	Insol	Insol	4	Insol	Insol	Insol	Insol
Ethyl ether	109	115	∞	46	Insol	13		14
Ethyl acetate	30	24	{ *5 3	*7	Insol	1	{ *7 4	
Amyl nitrate	84	39	51	Insol	Insol	7		16
Amyl acetate	133	37	86	Insol	Insol	1		Insol
Benzol	48	36	71	35	Insol	18		12
Toluol	39	33	72	57	0.09	Very sol		14
Turpentine	115	116	60	65	15	Very sol		29
Nitrobenzene	39	24	9	14	{ *12 Insol	Insol		3
Aniline	3	Insol	{ *33 Insol	Insol	{ *2 Insol	Insol		Insol
Chloroform	10	23	54	33	{ *1.5 0.96	∞		83
Carbon disulfide	∞	∞	∞	55	13.45	∞	Very sol.	
Carbon tetrachloride	∞	∞	44	30	36.00	1.8	∞	12
62° Naphtha	Very sol	63	5		6.80	2.8	7	18
Ethyl alcohol	Insol.	Insol.	Insol.	{ *1 Insol	Insol	Insol	Insol	Insol
Propyl alcohol	Insol.	Insol.	{ *1 Insol	{ *11 Insol	Insol	Insol	Insol	Insol

Numbers refer to grams soluble in 100 grams cold solvent.

* Grams soluble in 100 grams boiling solvent.

Table IV gives the results of the fractional distillations of the hydrocarbons. A number of distillations at reduced pressure were tried, but the results were not satisfactory, and work along this line was discontinued for lack of time. It was noticed, however, that (1) gilsonite is soluble in its own distillate and in those from wurtzilite and tabbyite, (2) tabbyite is soluble in the distillates from gilsonite and wurtzilite, but (3) wurtzilite is insoluble in its own distillate and in the distillates from gilsonite and tabbyite. Gilsonite is soluble in stearin and hot paraffin, but wurtzilite is insoluble in both of these materials.

TABLE IV

Substance	Trin.	Ber.	Gils.	Tab.	Wur. I	Ozok.	R. A.
0-150° C.....	14.93	9.89	9.34	3.12	16.15	0.21	0.91
150-200° C.....	10.42	7.99	5.34	11.93	21.70	8.91	3.22
200-250° C.....	2.26	16.08	12.84	24.87	22.82	8.38	0.29
250-300° C.....		21.12	28.99	13.21	0.91	17.69
300-350° C.....				4.77		25.89
350-400° C.....						26.85
Total volatile.....	27.61	55.08	56.51	57.90	61.58	87.93	4.42
Fixed carbon.....	36.69	39.60	43.13	37.45	36.92	10.03	7.53
Ash.....	35.70	5.32	0.36	4.65	1.50	0.04	88.05
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

CONCLUSIONS

The marked differences in the physical and chemical properties and in the compositions of the five hydrocarbons are established. Tabbyite is shown to be a distinct substance. The reported insolubility of wurtzilite is amply confirmed.

UNIVERSITY OF UTAH
SALT LAKE CITY

WINKLER'S METHOD FOR THE DETERMINATION OF OXYGEN IN WATER; THE EFFECT OF NITRITE AND ITS PREVENTION¹

By FRANK E. HALE AND THOMAS W. MELIA

The accuracy of Winkler's method² for the determination of dissolved oxygen in water under usual conditions has been shown by many investigators. Comparison with Bunsen's direct estimation of the oxygen by boiling off the gas and determining the amount by gasometric analysis was carefully made by Winkler, himself, and later by Chlopin,³ by Gill,⁴ and by Birge and Juday.⁵

EFFECT OF NITRITE AND ITS CORRECTION

Considerable criticism has arisen of late regarding the Winkler method because of the effect of nitrites upon the results. If the effect were quantitative, a correction could be applied according to the following formula:

$$\text{H}-\text{O}-\text{N}=\text{O} + \text{H}-\text{I} = \text{H}-\text{O}-\text{H} + \text{N}=\text{O} + \text{I}$$

in which N is equivalent to I and to $\frac{1}{2}\text{O}$, and each part per million of nitrogen as nitrite would increase the apparent oxygen content by $\frac{8}{14} \times 1$ or 0.57 p. p. m.

But the reaction is catalytic, the $\text{N}=\text{O}$ taking up oxygen from the air to again form nitrous acid so that the effect under certain conditions may be considerable.

The present experiments were undertaken to ascertain the extent of the error with varying amounts of nitrite and if possible to find a simple method of prevention.

It is hardly necessary to describe the Winkler method as the details are in many text-books. The water to be examined, in our work, was poured through a funnel, keeping the funnel full, to the bottom of 300 cc. bottles, having tight fitting, well ground glass stoppers, and overrun until all water in contact with air in the bottle was removed. Then 1 cc. of a nitrite solution was introduced by a pipette at the bottom, the stopper inserted so as to exclude any air bubbles and the oxygen determined. In order to keep conditions alike a solution of nitrite was made of such strength that it contained 500 p. p. m. of nitrite, expressed as nitrogen. Varying quantities of this solution were then made up to 10 cc. and 100 cc. volumes from which 1 cc. was introduced into the bottles according to the amount of nitrite desired. Table I shows the amounts needed.

The results were tested by the usual colorimetric method of Griess and found to be correct.

In the determination of the oxygen the manganous sulfate and the potassium hydroxide-potassium iodide solutions were carefully measured, 2 cc. of each being introduced at the bottom of the bottle so as to displace an equal amount of the water tested. The bottle was well shaken and the precipitate allowed to

¹ Paper presented at the 48th meeting of the American Chemical Society, Rochester, September 8-14, 1913.

² L. W. Winkler, *Ber. d. chem. Ges.*, **21**, 2843 (1888); **22**, 1764 (1889).

³ Chlopin, *Archives f. Hygiene*, **27**, 18 (1896).

⁴ Report of Metropolitan Sewerage Commission, N. Y., 401 (1910).

⁵ Birge and Juday, *Wisconsin Survey Bulletin*, **22**, 11, 12 (1911).

TABLE I—NITRITE SOLUTIONS

Amount of original sol.		Nitrite p. p. m.
0.6 cc.	diluted to 100 cc.	0.010
1.2 cc.		0.020
1.8 cc.		0.030
2.4 cc.		0.040
3.0 cc.		0.050
0.6 cc.	diluted to 10 cc.	0.100
1.2 cc.		0.200
1.8 cc.		0.300
2.4 cc.		0.400
3.0 cc.		0.500
0.6 cc.	added to 300 cc.	1.000
1.2 cc.		2.000
1.8 cc.		3.000
2.4 cc.		4.000
3.0 cc.		5.000

settle well before adding the acid. Hydrochloric acid, concentrated, reacts most quickly. About 2 cc. are needed. This is also better introduced at the bottom because the catalytic nitrite action can take place only in acid solution and in the presence of air. Correction for displacement is required only for the first two solutions. The titrations were made upon 100 cc. using $N/100$ thiosulfate.

The following table shows the effect of varying quantities of nitrite upon the oxygen determination:

TABLE II—SHOWING EFFECT OF NITRITE

Nitrite p. p. m.	Water used	Cc. $N/100$ thiosulfate per 100 cc.	Oxygen p. p. m.	Differences p. p. m.
0.003	Brooklyn tap	12.70	10.31	..
0.010	Brooklyn tap	12.60	10.23	-0.08
0.020	Brooklyn tap	12.70	10.31	±0.00
0.030	Brooklyn tap	12.60	10.23	-0.08
0.040	Brooklyn tap	12.60	10.23	-0.08
0.050	Brooklyn tap	12.55	10.19	-0.12
...	distilled	13.10	10.64
0.100	distilled	13.15	10.68	+0.04
0.100	distilled	13.20	10.72	+0.08
0.200	distilled	13.30	10.80	+0.16
0.200	distilled	13.50	10.96	+0.32
0.300	distilled	13.00	10.56	-0.08
0.300	distilled	13.60	11.04	+0.40
0.400	distilled	13.60	11.04	+0.40
0.500	distilled	13.70	11.12	+0.48
1.000	distilled	15.50	12.58	+1.94

It will be seen from these results that the effect of nitrite is inappreciable with amounts below 0.200 p. p. m. and the ordinary run of waters rarely contain sufficient nitrite to affect the accuracy of the results. Winkler himself placed the danger point at 0.100 p. p. m. nitrite.

As the nitrite is increased the end reaction is not permanent and the starch blue color comes back so quickly that considerable error is caused. That the action is catalytic and accumulative is shown by the following facts:

A sample with 0.500 p. p. m. nitrite kept three days tightly stoppered after the reagents had been added ready to titrate gave the same result as above, the error, 0.48 p. p. m., occurring during titration. The same sample kept three days exposed to air required 21.3 cc. $N/100$ thiosulfate, equivalent to 17.30 p. p. m. oxygen, an error of 6.66 p. p. m. A sample with 1.000 p. p. m. nitrite kept three days in acid condition in contact with air required 23.85 cc. thiosulfate, equivalent to 19.37 p. p. m. oxygen, an error of 8.73 p. p. m.

Winkler,¹ and also Max Müller,² tried to correct the error by adding acid and iodide and making a separate titration and correction, but this could not accomplish the result since the reaction is catalytic and varies with the time of exposure to the air. Rideal and Stewart³ in 1901 recommended preliminary treatment with permanganate in acid condition and neutralization of excess permanganate by oxalate to eliminate the nitrite error. Rideal and Burgess⁴ advised a colorimetric method in 1909 in the bottle, correcting for nitrite.

As nitrite may be oxidized and quantitatively determined by permanganate by the method of Kinnicutt and Nef⁵ it was hoped that by allowing for a certain length of time contact in alkaline condition before acidifying, the manganese oxyhydrate could be made to destroy the nitrite and introduce thereby a known error. The following table gives the results of our experiments, using distilled water:

TABLE III—SHOWING RESULTS AFTER STANDING IN ALKALINE CONDITION

Nitrite p. p. m.	Time in alkaline condition	Cc. $N/100$ thiosulfate per 100 cc.	Oxygen p. p. m.	Difference p. p. m.
...	3 hours	11.40	9.26	..
...	3 hours	11.40	9.26	..
...	18 hours	11.38	9.24	-0.02
...	18 hours	11.42	9.27	+0.01
1.000	0 hour	14.50	11.77	+2.51
1.000	1/4 hour	14.20	11.53	+2.27
1.000	1/2 hour	16.00	12.99	+3.73
1.000	1 hour	14.70	11.94	+2.68
1.000	1.5 hours	14.90	12.10	+2.84
1.000	2 hours	14.80	12.02	+2.76
1.000	18 hours	15.20	12.34	+3.08

This procedure failed completely as the errors remained high and irregular.

The next attempt was to try a weaker acid, acetic, instead of hydrochloric. This gave unsatisfactory results since the precipitate would not readily entirely dissolve even though a large excess of acid was added to the portion titrated. But as the results were not high the procedure was modified by adding hydrochloric acid to dissolve the precipitate, being careful to exclude all air, then crystals of sodium acetate were introduced quickly to neutralize the hydrochloric acid and render the solution acid with acetic acid. After the solution contains only free acetic acid it may be exposed to the air without any danger of nitrite interference. The color never comes back. The end reaction is slightly slower in titration but not so as to appreciably lengthen the operation, simply requiring a little care not to overrun the end point. It was found that 2 cc. of hydrochloric acid, introduced at the bottom of the bottle to prevent the acidified solution coming in contact with air, was sufficient to dissolve all of the precipitate, and 4 grams of sodium acetate crystals would neutralize the excess of hydrochloric acid added and produce sufficient free acetic acid to bring about a proper reaction. As the crystals entrained air, it was feared that a slight error might be introduced in that way, but such did not

¹ L. W. Winkler, *Ber. d. chem. Ges.*, **21**, 2843 (1888); **22**, 1764 (1889).

² Max Müller, *J. Soc. Chem. Ind.*, **8**, 923 (1889).

³ S. Rideal and C. G. Stewart, *Analyst*, **26**, 141 (1901).

⁴ Rideal and Burgess, *Ibid.*, **34**, 193 (1909).

⁵ Sutton, "Volumetric Analysis," 10th Edition, p. 288.

seem to be the case as the solution contained free acetic acid before the air affected the nitrite. Pellets were compressed containing 4 grams of sodium acetate and tried also, but while the results were as accurate the pellets dissolved very slowly and introduced just as much air. The crystals were tried with the idea of displacing as little liquid as possible, but both crystals and pellets displace three cc. of solution for which correction must be made as it contains iodine previously set free by the hydrochloric acid. The following table gives the results of these experiments:

TABLE IV. SHOWING RESULTS WITH SODIUM ACETATE CRYSTALS

Nitrite p. p. m.	Acid used	Sodium acetate 4 grams	End reaction	Cc. N/100 thio-sulfate per 100 cc.	Oxygen p. p. m.	Difference	Remarks
1.0	4 cc. HCl conc. (a)	crystals	sharp	11.15	9.05	..	Blank
1.0	Acetic conc. (a)	crystals	uncertain	11.00	8.93	-0.12	Failure
1.0	4 cc. HCl conc. (a)	crystals	returned	14.00	11.48	+2.43	Excess HCl
1.0	4 cc. HCl 1:1 (a)	crystals	sharp	11.30	9.26	+0.21	
1.0	2 cc. HCl 1:1 (b)	crystals	sharp	11.00	9.02	-0.03	
...	4 cc. HCl 1:1 (a)	10.90	8.85	-0.05	Blank
...	4 cc. HCl 1:1 (a)	11.02	8.95	+0.05	Blank
...	4 cc. HCl 1:1 (a)	crystals	sharp	10.85	8.90	...	Blank
1.0	4 cc. HCl 1:1 (a)	crystals	sharp	11.24	9.22	+0.32	
0.5	4 cc. HCl 1:1 (a)	pellet	sharp	11.00	9.02	+0.12	
1.0	4 cc. HCl 1:1 (a)	pellet	sharp	11.22	9.20	+0.30	
2.0	4 cc. HCl 1:1 (a)	pellet	sharp	11.15	9.14	+0.24	
5.0	4 cc. HCl 1:1 (a)	pellet	sharp	11.03	9.05	+0.15	
...	2 cc. HCl conc. (b)	11.00	8.93	-0.09	Blank
...	2 cc. HCl conc. (b)	crystals	sharp	11.00	9.02	...	Blank
1.0	2 cc. HCl conc. (b)	crystals	sharp	10.65	8.74	-0.28	
1.0	2 cc. HCl conc. (b)	crystals	sharp	11.20	9.18	+0.16	Excess starch
1.0	2 cc. HCl conc. (b)	crystals	sharp	10.90	8.94	-0.08	Little starch
1.0	2 cc. HCl conc. (b)	crystals	sharp	11.05	9.06	+0.04	Careful end-point

(a) Acid added at top of bottle.

(b) Acid added at bottom of bottle.

It will be noticed that when the acid was added at the top of the bottle there was a slight tendency for a positive error. This was counteracted by adding the acid at the bottom of the bottle, as shown in last results.

Some of the above solutions were allowed to stand over night in contact with air and were then again titrated. All gave considerably lower results, not varying with the amount of nitrite, 1-5 p. p. m., but constant, showing a complete prevention of the nitrite reaction, and also showing that solutions acidified ready for titration should not stand in contact with air for several hours before titrating.

In order to further simplify the procedure a strong solution of potassium acetate (which is much more soluble than the sodium salt) was made by dissolving 100 grams of the crystals in 25 cc. of hot water and filtering. The crystals increased the volume to about 80 cc. At first this syrup was used. Later the syrup was diluted to 100 cc. This makes a stable solution, 1 cc. of which contains 1 gram of potassium acetate.

The following table shows the excellent results obtained in the presence of 1 p. p. m. nitrite with the use of this potassium acetate solution.

TABLE V. SHOWING RESULTS WITH POTASSIUM ACETATE SOLUTION

Nitrite p. p. m.	Acid used	Potassium acetate solution	End reaction	Cc. N/100 thio-sulfate per 100 cc.	Oxygen p. p. m.	Difference
2 cc.	HCl conc.	1 cc. = 10.4 grams	sharp	9.5	7.70	-0.03
2 cc.	HCl conc.	1 cc. = 10.4 grams	sharp	9.5	7.73	...
1	2 cc. HCl conc.	1 cc. = 10.4 grams	returned	9.5	7.73	+0.00
1	2 cc. HCl conc.	1 cc. = 10.4 grams	returned	9.7	7.90	+0.17
1	2 cc. HCl conc.	2 cc. = 20.8 grams	sharp	9.5	7.77	+0.04
1	2 cc. HCl conc.	2 cc. = 20.8 grams	sharp	9.3	7.61	-0.12
1	2 cc. HCl conc.	2 cc. = 2 grams	sharp	9.6	7.85	+0.12

(b) Acid added at bottom of bottle.

NOTE.—Since this paper was written the method has been used by the Sewer Bureaus of N. Y. City in a study of N. Y. harbor. Several hundred determinations have been made with nitrite sometimes as high as 2 p. p. m., with entire satisfaction.

EFFECT OF ORGANIC MATTER

It is also claimed that the Winkler method cannot give accurate results in the presence of organic matter. Hefelmann and Barth¹ make this criticism of Müller's method which appears to be identical with Winkler's. The same criticism has been made as to sewage.

The writers have found no appreciable difference in results to be caused by heavy microscopic growths in water, and the following experiments were undertaken to ascertain to what extent the results might be lowered by either oxidation or direct combination of iodine with the organic matter present in sewage. The sewage employed contained total solids 950 p. p. m., loss on ignition 340 p. p. m., fixed solids 610 p. p. m., chlorine 185 p. p. m., free ammonia 13.6 p. p. m., albuminoid ammonia 8.0 p. p. m., and was taken from a Brooklyn sewer at Atlantic Ave. and Clinton St.

In a preliminary experiment 0.1 cc. of N/100 iodine when added to 25 cc. of sewage containing 1 cc. each of manganous sulfate solution and concentrated hydrochloric acid gave a deep blue with starch solution which did not fade out in thirty minutes.

Bottles of 300 cc. capacity were then filled as for oxygen determination with the sewage, 2 cc. of manganous sulfate solution added, 2 cc. of concentrated hydrochloric acid, and then N/100 iodine added. After standing stoppered five and also thirty minutes, 100 cc. portions were titrated with N/100 thiosulfate. The loss of iodine, expressed as parts per million of equivalent oxygen, was inappreciable, at least not over 0.2 p. p. m. Upon standing in presence of air over night, even, no more iodine was used up apparently since an increased amount of iodine was present, due to the effect of the nitrite in the sewage.

The experiment was then tried in a different manner. The oxygen was determined in distilled water, the sewage, and mixtures of the two containing 10%, 25%, and 50% of sewage. These mixtures were obtained by filling the bottle with distilled water through a funnel, as previously described, and then adding by pipette at the bottom the required amount of sewage, forcing out distilled water at the top.

The results were within experimental error. The starch blue color returned after titration showing the presence of some nitrite but there was not sufficient to affect the accuracy of the results.

¹ R. Hefelmann and K. Barth, *Chem. Ztg.*, **13**, 1337 (1889).

The experiment was repeated on 10% sewage mixtures containing an addition of 1 p. p. m. nitrite with and without the use of potassium acetate solution. As was to be expected, the results were high without the acetate and within experimental error with the acetate.

The following table gives the results of these experiments:

TABLE VI—SHOWING LACK OF EFFECT OF ORGANIC MATTER

Liquid	Cc. HCl conc.	Cc. K acetate, 1 cc. = 1 gram	Cc. mm. sulfate	Nitrite p. p. m.	Cc. N 100 iodine per 100 cc.	Time min.	Cc. N 100 thiosulfate per 100 cc.	Oxygen p. p. m.	Oxygen theory p. p. m.	Difference as oxygen	End reaction
Sewage.....	2	2	2	2.3	5	2.00	-0.24	ret.
Sewage.....	2	2	2	2.3	30	2.05	-0.20	ret.
Sewage.....	2	2	2	4.6	5	4.75	+0.12	ret.
Dist. water...	2	2	2	9.60	7.80	7.80	sharp
Sewage 10%...	2	2	2	8.80	7.15	7.22	..	-0.07	ret.
Sewage 25%...	2	2	2	7.55	6.13	6.36	..	-0.23	ret.
Sewage 50%...	2	2	2	6.00	4.87	4.91	..	-0.04	ret.
Sewage 100%...	2	2	2	2.50	2.03	2.03	ret.
Sewage 10%...	2	2	1	9.85	8.00	7.22	..	+0.78	ret.
Sewage 10%...	2	1	2	1	..	9.15	7.45	7.22	..	+0.23	ret.
Sewage 10%...	2	2	2	1	..	8.45	6.91	7.22	..	-0.31	sharp

PRESERVATION OF SAMPLES

Some experiments were also carried out to determine the possibility of preserving samples of water for oxygen determination unchanged so that they may be transported to a laboratory for analysis. Birge and Juday¹ give some results on samples which stood up to six hours. They also quote Spitta,² Gill,³ Seyler⁴ and Dost,⁵ that the oxygen does not change greatly in 24 hours, even with a 10° rise in temperature, with exposure to the air, and though the water become supersaturated.

TABLE VII—SHOWING RESULTS WITH USE OF BULB PIPETTE AND STORAGE

Source of sample	Time of standing	Temperature	Cc. N/100 thiosulfate per 100 cc.	Oxygen p. p. m.	Remarks
Mt. Prospect Res. 12 foot depth.....	15.5° C.	15.10	12.26	Supersaturated
Mt. Prospect Res. 12 foot depth.....	1 1/2 hours	25° C.	14.40	11.73	Supersaturated
Mt. Prospect Res. 12 foot depth.....	18 hours	25° C.	13.00	10.56	Supersaturated 8.35 saturation
Mt. Prospect Res. 12 foot depth.....	15.5° C.	15.95	12.95	10.04 saturation
Mt. Prospect Res. 12 foot depth.....	1 3/4 hours	13° C. (icebox)	16.05	13.03	
Mt. Prospect Res. 12 foot depth.....	20 hours	13° C. (icebox)	15.55	12.63	
Gowanus canal.....	2 hours	room	0.00	0.00	

From our experience it seems preferable to make determinations on the field, but satisfactory results may be obtained by using the device that D. D. Jackson⁶ recommends for putrescibility bottles, that is, a medicine pipette passing through a rubber stopper. If the samples are below saturation with oxygen, the bulb may be collapsed and the sample transported without ice, but if the samples are saturated or supersaturated with oxygen the bulbs should be left filled

with the water and the samples iced. The bulbs take care of the change in volume and thus prevent loosening of the stopper and consequent leakage of air. The icing holds the excess oxygen of supersaturated samples in solution. Samples of sewage should preferably be iced to prevent loss of oxygen by combination with the organic matter present, and also preserved by 1 cc. of 40% formaldehyde as recommended by A. Lederer.¹ The samples should be collected in the usual way by passing the water to be examined through the bottle until all water in contact with air is removed. The bulb should be filled with some of the same water from a dish and all air carefully forced out of the bulb with the pipette pointed upward. It is then quickly inserted in the filled bottle, which has been protected by a glass stopper until now, and either left full or collapsed according as the samples are iced or not, respectively. The effect of exposure to air of the water which fills the bulb is inappreciable, but the presence of any air bubbles would be serious.

Table VII gives some results with water so collected and stored.

The first three supersaturated samples lost oxygen upon storing at room temperature exposed to diffused daylight, although the sample kept 18 hours still contained more than 2 p. p. m. oxygen over saturation at room temperature. Bubbles of gas could be seen collected under the stopper.

The ice-box samples kept very well even though containing about three parts of oxygen over saturation. The three samples were of course taken separately at as near the same depth and spot as possible.

Samples low in oxygen keep perfectly without ice.

SUMMARY

I. Winkler's method for dissolved oxygen in water is very easy, rapid and accurate. Duplicate samples

in routine work ordinarily check within 0.1 p. p. m. oxygen.

II. Nitrite as present in the usual run of waters has no appreciable effect upon the accuracy of the results.

III. Nitrite in quantities upward of 0.2 p. p. m. increases the results by a catalytic reaction, increasing with increasing amounts of nitrite.

IV. The effect of high nitrite present in any amount ever occurring in water may be counteracted by the use of potassium acetate solution (or sodium acetate crystals) to neutralize the hydrochloric acid before exposure to the air.

¹ Lederer, "The Influence of Storage and Various Preservatives upon the Dissolved Oxygen in Waters," Sewage Disposal Investigations, the Sanitary District of Chicago, 1910.

¹ Birge and Juday, *Wisconsin Survey Bulletin*, **22**, 17, 18 (1911).

² Spitta, *Archives f. Hygiene*, **38**, 215 (1900).

³ Gill, *Tech. Quart.*, **6**, 250 (1892).

⁴ Seyler, *Chem. News*, **67**, 87 (1893).

⁵ Dost, *Chem. Centralbl.*, **77**, 1457.

⁶ D. D. Jackson and W. A. Horton, *This Journal*, **1**, 338 (1909).

The procedure then is to add at the bottom of the bottle 2 cc. of manganous sulfate solution (480 grams per liter) followed by 2 cc. of potassium hydroxide-iodide solution (360 grams hydroxide and 100 grams iodide per liter). Shake and settle. Add at the bottom 2 cc. concentrated hydrochloric acid and shake until the precipitate is entirely dissolved. Then add 2 cc. potassium acetate solution (1000 grams per liter) at the bottom and mix. Withdraw by pipette 100 cc. into an Erlenmeyer flask and titrate with *N*/100 thiosulfate, adding a little starch solution at the end. Correction must be made for 6 cc. of water displaced by the first two solutions and by the acetate solution. The acid needs no correction, since it displaces only water from which oxygen has been removed.

Precautions must be taken to exclude contact with air as much as possible until the solution is ready to titrate by replacing the stopper as quickly as possible after each reagent is introduced; to get complete solution of the precipitate by the hydrochloric acid; to give the thiosulfate a little more time to react at the end point in the acetic acid condition; to use small amounts of starch solution. For introducing the solutions it is advisable to use pipettes with two marks, measuring 2 cc., well up on the pipette so as to give head and not contaminate the upper liquid in the bottle more than necessary while actually displacing liquid from the bottle in proportion to the amount introduced.

V. Samples for oxygen may be taken and transported elsewhere for titration in ground glass stoppered bottles with part of the chemicals added, either in alkaline or acid condition, if kept out of contact with air. The alkaline condition is preferable, since changes in temperature cannot change results, all the oxygen being in the precipitate. In either condition if air leaks in it may increase results, in alkaline condition by direct absorption, in hydrochloric acid condition by catalytic action of nitrite. It is not advisable to add the acetate until ready for titration.

Samples for oxygen may best be transported elsewhere for determination by using medicine pipettes. If samples are not saturated with oxygen, the bulbs should be collapsed and samples transported without ice; if supersaturated the bulbs should be full of the water and samples iced.

Acknowledgment is due Mr. W. A. Horton for assistance in many of the determinations.

MT. PROSPECT LABORATORY
BROOKLYN, N. Y.

SULFUR DIOXIDE IN GELATINE¹

By PAUL POETSCHKE

Edible gelatin, according to the tentative standard prepared by the Committee on Food Standards of the Association of Official Agricultural Chemists, is the purified, dried, inodorous product of the hydrolysis, by treatment with boiling water, of certain tissues, as skin, ligaments, and bones, from sound animals, and contains not more than two (2%) per cent of ash and not less than fifteen (15%) per cent of nitrogen. It

is used extensively in the preparation of various articles of food, such as jellies, jams, candy and ice cream, and it is, therefore, of importance to eliminate, as far as possible, all contaminating chemical substances.

Sulfur dioxide was formerly employed as a bleaching agent and also in the treatment of the raw materials used in the manufacture of gelatin, with the result that the finished product contains considerable quantities of this substance. It was not until the Food and Drugs Act of June 30, 1906 went into effect, that the attention of food chemists was seriously directed to the determination of this substance, not only in gelatin but also in other food materials such as wine, dried fruits and sugar products. The products in which sulfur dioxide was used were readily distinguishable on account of the considerable amounts present, but as the use of this substance was discontinued in all stages of manufacture, the problem became more difficult, since sulfur dioxide was still found in gelatin prepared without the use of this substance. The origin of the sulfur dioxide found by analysis, then became a recurring question and the opinion of many manufacturers and chemists was that the existing methods of analysis gave inconsistent and fallacious results. The main object of the present investigation was to determine the sources of error involved in the determination of sulfur dioxide and to develop a uniform and satisfactory method of analysis. Incidentally, the origin of the relatively small quantities of sulfur dioxide found in gelatin prepared without the addition of this substance was taken up.

EXPERIMENTAL PART—ANALYTICAL

Owing to the wide discrepancies which were observed in the determination of SO_2 in gelatin, when the same sample was analyzed by different chemists, an investigation of the cause of these discrepancies was undertaken. Much experimental work was required and, therefore, the various sources of error are taken up in detail.

In the distillation method, a known weight of the sample is dissolved in water and distilled, after the addition of phosphoric acid, in an atmosphere of CO_2 . The distillate is collected in an excess of iodine and the iodine used up in oxidizing the SO_2 determined volumetrically or the resulting H_2SO_4 determined gravimetrically as BaSO_4 . Bromine water is also used as an oxidizing agent, but in this case the gravimetric method is employed.

I—ADVANTAGES OF GRAVIMETRIC OVER VOLUMETRIC METHOD

The gravimetric method of estimation of the sulfuric acid formed is the best method, since the volumetric method, in which the excess iodine is titrated with a solution of sodium thiosulfate, is subject to considerable error owing to the possible presence of reducing substances other than SO_2 , which may come over with the distillate. A comparison of the gravimetric and the official volumetric method¹ on a sample of gelatin gave the following result:

¹ Presented at the 48th meeting of the A. C. S., Rochester, September 8-12, 1913.

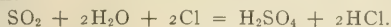
¹ U. S. Dept. of Agric., Bur. of Chemistry, Bull. 107.

	Gravimetric Per cent	Volumetric Per cent
Sulfur dioxide.....	0.0085	0.0102

Owing to the fact that the sample contained a small quantity of SO_2 , a $N/50$, instead of a $N/10$, iodine solution was used. This sample was selected for this purpose since the influence of reducing substances is rendered more apparent when the SO_2 is low. The result on this sample demonstrates that reducing substances are evolved and that these are a source of error to be avoided. It has been repeatedly observed that the iodine containing distillates becomes turbid, in some cases the cloudiness is very marked, and this in itself is evidence of the fact that the error introduced will depend entirely upon the nature of the sample under examination.

II—HYDROCHLORIC ACID USED FOR GENERATING CARBON DIOXIDE

Commercial HCl is frequently used for generating CO_2 from marble. It is absolutely necessary to use chemically pure acid for this purpose since the commercial acid contains free chlorine. In a number of experiments it was found that free chlorine could be detected in the distilling flask by means of starch iodide when commercial HCl was used, even though the CO_2 was washed by bubbling through a wash bottle containing dilute copper sulfate solution. The free chlorine would naturally oxidize an equivalent amount of SO_2 in accordance with the following equation:



III—ADVANTAGES OF IODINE OVER BROMINE

In the gravimetric determination of SO_2 , iodine is preferable to bromine since it does not oxidize H_2S to H_2SO_4 . Horne¹ separated the H_2S by passing the distillate through a 2 per cent neutral solution of cadmium chloride and states that the SO_2 is not precipitated but passes on to the iodine, where it is oxidized to H_2SO_4 , to be afterwards precipitated as BaSO_4 . The fact is that when the gravimetric method is employed using iodine as the oxidizing agent, it is not necessary to remove H_2S . This is, however, a necessary precaution when the volumetric method is used. When H_2S is passed into an iodine solution the following reaction takes place:



Two experiments were conducted in order to verify this reaction, especially as to the possibility of oxidizing some of the H_2S to H_2SO_4 .

1. 50 cc. of $N/20$ iodine solution were diluted to 200 cc. with distilled water and a current of H_2S passed into the solution until it was decolorized; 5 cc. of concentrated HCl were then added, the solution concentrated to about 75 cc. by boiling, filtered and precipitated with BaCl_2 . BaSO_4 obtained = 0.0023 gram.

2. This experiment was conducted in the same manner except that the HCl was added before passing in H_2S . BaSO_4 obtained = 0.0020 gram.

A blank determination conducted by diluting 50 cc. of iodine solution to 200 cc. with water and boiling down to 75 cc., filtering and precipitating with BaCl_2 , gave 0.0008 gram of BaSO_4 .

¹ "The Chemical Determination of Sulfites in Sugar Products," U. S. Dept. Agr., Bur. of Chemistry, *Bull.* 105.

Taking the average BaSO_4 obtained in Experiments 1 and 2 and deducting the blank, we have 0.0014 gram of BaSO_4 , equivalent to 0.0004 gram of SO_2 . Considering the quantity of H_2S passed through the iodine and also the fact that no attempt was made to purify the gas, it is evident that the amount of BaSO_4 is negligible and that these facts show that none of the H_2S is oxidized to H_2SO_4 .

When H_2S is passed into a solution of bromine, sulfur is first precipitated but further oxidation to H_2SO_4 takes place. This was verified by diluting 50 cc. of saturated bromine water to 200 cc. with water and passing in H_2S until the solution was decolorized. The liquid was then acidified with 5 cc. of HCl , concentrated to 75 cc. by boiling, filtered and precipitated with BaCl_2 . A heavy precipitate of BaSO_4 was obtained, indicating that bromine water oxidizes H_2S to H_2SO_4 .

That bromine oxidizes H_2S and other volatile sulfur compounds, thus yielding high results for SO_2 , is evident from the following experiment: A pound of fresh round steak was freed from fat and passed through a meat chopper. A determination of SO_2 on the same day by the gravimetric-iodine method gave two (2) parts of SO_2 per million. The meat was allowed to decay and on the fourth day another determination by the same method gave six (6) parts per million. On the ninth day the meat had a strongly ammoniacal odor. Two determinations were made, one by the gravimetric iodine method and the other by substituting saturated bromine water for the iodine solution. Blank determinations were made in both cases. The following results were obtained:

	Sulfur dioxide in parts per million
With iodine.....	11
With bromine.....	37

Winton and Bailey¹ obtained similar results by distillation of beef which was allowed to decompose. They collected the distillate in bromine after first passing through a dilute solution of copper sulfate in order to remove sulfides and mercaptans, the resulting copper sulfide being weighed and reported as H_2S . In two separate series of experiments on beef which was allowed to decompose for nine days (calculating their H_2S figures to SO_2) they obtained as follows:

	Sulfur dioxide in parts per million	
	1	2
Obtained by copper sulfate..	38	8
Obtained by bromine.....	12	10
Total, 50	50	18

The authors found that the amount of sulfur as H_2S was larger than the amount of sulfur as SO_2 , especially in the case of veal.

It is, therefore, obvious that iodine is preferable to bromine since it is not necessary to pass the distillate through a solution of a metallic salt, such as copper sulfate or cadmium chloride, in order to remove sulfides when iodine is used.

¹ *J. Am. Chem. Soc.*, **29**, 1499 (1907).

IV—DISSOLVING THE GELATIN

The fact that gelatin is insoluble in cold water, but swells up in it, and is readily soluble in hot water, naturally leads some analysts to use hot water in order to facilitate solution and to prevent the flask containing the mixture of gelatin and water from breaking, which frequently results if the flask is heated directly over a small flame before the gelatin is completely dissolved. The addition of hot water, although the flask is quickly stoppered, causes a loss of SO_2 . The results of three determinations on a sample of gelatin which was finely ground and well mixed, gave the following:

Per cent sulfurous acid	a. 0.0350
	b. 0.0350
	c. 0.0355

The same sample of gelatin was treated in exactly the same way, except that instead of adding cold, recently boiled distilled water, hot water was used, the flask connected to the apparatus and the usual distillation carried out. It usually required from five to ten minutes to dissolve the gelatin and during this time the flask was stoppered. The loss of SO_2 incurred by this treatment is apparent from the following three determinations:

Per cent sulfurous acid	a. 0.0247
	b. 0.0265
	c. 0.0212

The above results show that a loss of from 25 to 40 per cent of the total sulfurous acid occurs when hot water is used to dissolve the gelatin. The same sample of gelatin was sent to a large commercial laboratory and the following result was reported:

Per cent sulfurous acid = 0.0173.

It appears highly probable that hot water was used in this case to dissolve the gelatin, since the determination shows a loss of about 50 per cent of the total sulfurous acid.

V—CONCENTRATION OF THE DISTILLATE

Zerban and Naquin,¹ in their work on sulfurous acid in molasses, call attention to the fact that if it is necessary to concentrate the distillate, this should be done in flasks with narrow openings when gas is used as a source of heat for concentrating the distillate.

Kühn and Rühle² have conducted a series of experiments in which it was shown that when a solution of iodine is boiled over a gas burner in a beaker, contamination from the products of combustion of the illuminating gas takes place and this gives rise to serious errors. The conclusion is drawn that the SO_2 obtained in the distillation of meat is not due to its formation from sulfur compounds but to contamination from the surrounding atmosphere.

Repeated blank determinations, run on successive days, demonstrated that a variable contamination with sulfur took place, since careful tests of the reagents used failed to account for the BaSO_4 obtained in the blanks. The following experiments were conducted in order to trace this source of error:

¹ F. Zerban and W. Naquin, U. S. Dept. of Agriculture, Bureau of Chemistry, *Bull.* 116.

² *Z. Nahr. Genussm.*, 20, 10-9.

Several blank determinations were made by placing 300 cc. of recently boiled and cooled distilled water in the distilling flask (Fig. 1), phosphoric acid added and distilled in a current of CO_2 , collecting 200 cc. of distillate in a beaker containing 25 cc. of $N/10$ iodine solution. The beaker was kept closely covered with a clock glass provided with a hole in the center so as to fit over the exit tube of the condenser. The contents of the beaker were then acidified with 5 cc. of concentrated HCl , the solution boiled to expel the iodine and precipitated with 10 cc. of BaCl_2 solution. After standing over night the precipitate was filtered off and weighed as BaSO_4 .

Number	Date of experiment	Gram of barium sulfate obtained
1	Nov. 14, 1910	0.0045
2	Nov. 30, 1910	0.0054
3	Nov. 30, 1910	0.0067
4	Oct. 15, 1910	0.0016
5	Oct. 15, 1910	0.0016

Experiments 2 and 3 were run side by side, and including 1, on the same iodine solution. Experiments 4 and 5 were run on a new iodine solution.

The following experiments were conducted by direct precipitation, that is, 25 cc. of iodine solution, used in 4 and 5, were diluted to 100 cc., 5 cc. of concentrated HCl added, boiled to expel the iodine, and precipitated with BaCl_2 . Experiments 6 and 7 were run simultaneously, and 8 on the following day.

Number	Date of experiment	Gram of barium sulfate obtained
6	Oct. 15, 1910	0.0055
7	Oct. 15, 1910	0.0057
8	Oct. 16, 1910	0.0039

Two blank determinations were made using in one case a closely covered beaker as a receiver and in the second, the special "beaker-flask" shown in Fig. 1. The results were as follows:

Receiver	Gram barium sulfate obtained
Beaker.....	{ 0.0017 0.0052
"Beaker-flask".....	{ 0.0004 0.0004 0.0005

Table I gives a series of results, obtained by both methods, on samples of gelatin.

Sample No.	Barium sulfate Total		Barium sulfate Blank		Per cent sulfur dioxide in sample	
	Flask	Beaker	Flask	Beaker	Flask	Beaker
59344	0.0040	0.0117	0.0004	0.0052	0.0036	0.0065
59406	0.0041	0.0085	0.0004	0.0031	0.0037	0.0054
59551	0.0011	0.0043	0.0005	0.0037	0.0006	0.0006
59622	0.0014	0.0137	0.0004	0.0128	0.0010	0.0009
59647	0.0026	0.0103	0.0004	0.0049	0.0022	0.0054
59648	0.0015	0.0043	0.0005	0.0025	0.0010	0.0018
59800	0.0036	0.0164	0.0004	0.0078	0.0032	0.0086
59846	0.0045	0.0147	0.0009 ?	0.0135	0.0036 ?	0.0012
60008	0.0066	0.0127	0.0004	0.0057	0.0062	0.0070
60009	0.0049	0.0056	0.0004	0.0033	0.0045	0.0023

It is evident that the blank determinations made by collecting the distillate in beakers show very divergent results, whereas those collected in the "beaker-flasks" show excellent agreement, with the exception of the result on Sample 59846, in which case the blank is evidently too high, no doubt owing to accidental error since all of the determinations were conducted on the same iodine solution. While good agreement was obtained in several instances for percentage of SO_2 in the gelatin by both flask and "beaker-flask" when the corresponding blanks were deducted from the total BaSO_4 , it is impossible, even under these condi-

tions, when running blanks side by side, to obtain uniformly satisfactory results. It is, therefore, evident that the somewhat prevalent custom of running a blank once a day, or even that of running a blank with each determination, cannot be relied upon to give sufficiently accurate results when beakers are used to collect and concentrate the distillate. The uniformity of the blank results obtained with the "beaker flasks" demonstrates that contamination from the surrounding atmosphere is obviated in this case and it is, therefore, necessary to run a blank only with each change in the reagents.

The following duplicate determinations on two samples of gelatin show the uniformity of results obtained by providing against contamination from the surrounding atmosphere:

TABLE II

Sample number	Barium sulfite	Barium sulfite	Per cent sulfur dioxide in sample
	Total	Blank	
63181 <i>a</i>	0.0155	0.0004	0.0151
<i>b</i>	0.0146	0.0004	0.0142
63182 <i>a</i>	0.0260	0.0004	0.0256
<i>b</i>	0.0263	0.0004	0.0259

VI—COMPARISON OF STEAM DISTILLATION AND DIRECT DISTILLATION

Gudeman¹ recommends distillation with steam in order to eliminate errors arising from decomposition due to concentration of the mass during distillation, on the ground that many food products normally contain sulfur compounds which yield volatile sulfur compounds on distillation with acids and that these are increased with corresponding increase in acidity and concentration of the mass.

A number of analyses were made in order to determine whether it is necessary to observe this precaution in the case of gelatin. In all cases the distillation was conducted in a current of carbon dioxide, using steam in one case and heating directly with a Bunsen burner, as in the usual method, in the analyses made for comparison. The same volume of distillate was collected in both methods. Table III gives the results of these determinations.

TABLE III

Sample number	Percentage sulfur dioxide by distillation		Variation from steam distillation
	With steam	Without steam	
26226	<i>a</i> 0.1661	<i>a</i> 0.1723	+0.0034
	<i>b</i> 0.1678	<i>b</i> 0.1570	
		<i>c</i> 0.1707	
	Average = 0.1669	Average = 0.1703	
26227	<i>a</i> 0.0885	<i>a</i> 0.0886	+0.0017
	<i>b</i> 0.0862	<i>b</i> 0.0894	
	Average = 0.0873	Average = 0.0890	
26229	0.0277	0.0252	—0.0025
25915	0.0375	0.0374	—0.0001
26795	0.0618	0.0637	+0.0019
26796	0.0247	0.0257	+0.0010
26797	0.0130	0.0121	—0.0009
26798	0.0504	0.0516	+0.0012
26890	0.2732	0.2749	+0.0017
26885	0.0812	0.0828	+0.0017
26884	0.1084	0.1098	+0.0014
60232	0.0009	0.0000	—0.0009
60233	0.0000	0.0002	+0.0002
60234	0.0000	0.0010	+0.0010
60471	0.0027	0.0014	—0.0013
60419	0.0057	0.0072	+0.0015
61420	0.0026	0.0024	—0.0002
62123	0.0032	0.0042	+0.0010
62124	0.0048	0.0052	+0.0004

¹ THIS JOURNAL, 1, 81

The above analyses were conducted on routine samples of gelatin and it is very likely that the variations in the two methods are due to lack of uniformity in the samples. The variations occur in both directions and are not of sufficient magnitude to indicate that distillation with steam is necessary in the case of gelatin.

VII—RECOVERY OF KNOWN AMOUNTS OF SULFUR DIOXIDE

A number of experiments were made by distilling known amounts of sodium sulfite solution under the conditions observed in the regular method. It was necessary to prepare a solution of sodium sulfite and to measure aliquot portions, for standardization and distillation, at the same time so as to avoid oxidation. The standardization of the sulfite solution was carried out by titration in an atmosphere of CO₂, adding the sulfite solution to an excess of iodine and titrating the excess of iodine with sodium thiosulfate. The following results were obtained:

Sulfur dioxide by titration	Sulfur dioxide by gravimetric determination after distillation
Gram	Gram
0.0145	0.0145
0.0183	0.0170
0.0218	0.0207
0.0218	0.0206
0.0487	0.0482
0.0487	0.0477

VIII—METHOD OF CARRYING OUT THE DETERMINATION OF SULFUR DIOXIDE IN GELATIN

Apparatus Required.—Fig. 1 shows the apparatus and its arrangement in detail. Two units are represented, providing for two determinations which can

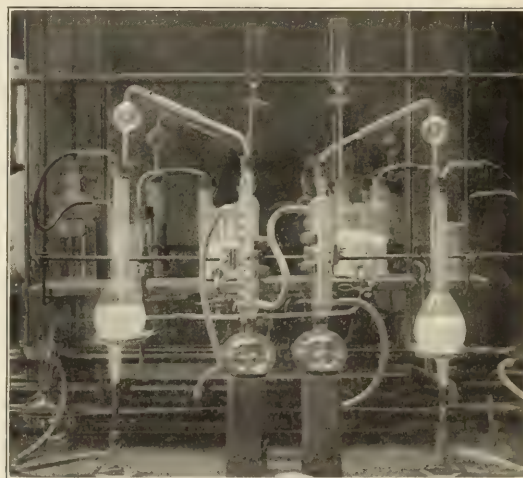


FIG. 1

be conducted at the same time. A Woulff bottle having two necks and an outlet at the bottom, fitted with a cylindrical open top, glass stoppered, long stem funnel, is used for generating the CO₂. The outlet tube at the bottom of the Woulff bottles is connected to a long tube leading to a reservoir for receiving the spent acid which is drawn off by opening the pinchcocks as required. The aforementioned

Woulff bottle is connected to a smaller one provided with two necks, this bottle serving to wash the CO_2 . The wash bottle is connected to the distilling flask, consisting of a long neck Kjeldahl flask of 500 cc. capacity, by means of a glass tube reaching to within $\frac{1}{2}$ inch of the bottom of the flask. The distilling flask is connected to the condenser through a Hopkins bulb. The glass tubes at the rubber connection are brought closely together and the tube leading into the condenser is extended so as to lead directly into the worm of the condenser. A special condenser was designed for this purpose, consisting of an eight-inch worm condenser provided with an exit tube 4 inches in length and $\frac{3}{4}$ inch internal diameter, so as to give a sufficient length of tube without requiring additional connections. The inlet tube of the condenser is $2\frac{1}{2}$ inches in length and $\frac{3}{4}$ inch internal diameter, and permits of convenient connection with the distilling bulb by means of a rubber stopper. A special receiving flask was designed, to serve also as a flask for concentrating the distillate and for precipitation of the H_2SO_4 . The main advantages of this "beaker-flask" have been discussed under V, but it is also efficient in avoiding contamination with sulfurous gases while the distillate is being collected and does not require transferring of the distillate to another receptacle for concentration. The flask is connected to the condenser by means of a paraffined flat cork having a small angular slit in the side to allow for the escape of the carbon dioxide. The "beaker-flask" has a capacity of 400 cc. and is 4 inches high. It is provided with a lipped neck $\frac{3}{4}$ inch high and $\frac{3}{4}$ inch in diameter.

Reagents Required.—1. Ordinary white marble broken into pieces small enough to pass through the neck of the Woulff bottle.

2. HCl for generating the CO_2 . Chemically pure concentrated HCl is diluted with an equal volume of water. Commercial HCl must not be used, owing to the presence of excessive amounts of free chlorine.

3. Phosphoric acid. Glacial phosphoric acid in sticks is broken into pieces weighing approximately 5 grams each.

4. Iodine solution. A $N/20$ solution.

5. HCl for acidifying the distillate. Chemically pure concentrated HCl.

6. BaCl_2 . An approximately $N/5$ solution, which should be perfectly clear and free from sediment.

7. Recently boiled and cooled distilled water.

NOTE.—Duplicate blank determinations are conducted on the reagents using the same amounts as in an actual analysis of gelatin. A label bearing the result of this standardization is placed on the iodine bottle and a corresponding correction is made in every determination. Two liters of iodine solution and a corresponding amount of the other reagents, except the distilled water, are set aside at one time for a series of analyses.

Determination.—Twenty-five cubic centimeters of iodine solution are measured into the receiving flask and the flask is connected to the condenser so that the end of the condenser reaches below the surface of the solution.

Twenty-seven and one-half grams of gelatin are weighed into the distilling flask and 300 cc. of dis-

tilled water added, together with a piece of phosphoric acid. The flask is then connected to the apparatus and the air is displaced by CO_2 generated by allowing the dilute HCl to fall upon the marble. The rate of flow of CO_2 is easily regulated by adjusting the flow of acid. When the air has been displaced, the gelatin is liquefied by immersing the flask in boiling water contained in a sauce pan, and the water is kept boiling until the gelatin is completely dissolved. Solution of the gelatin is facilitated by frequently agitating the flask by means of a rotary motion. When the gelatin is completely dissolved, the boiling water bath is removed, the flask dried and heat applied directly with a Bunsen burner.

A current of CO_2 is allowed to flow through the apparatus until the distillation is completed. When 200 cc. of distillate have been collected, the apparatus is disconnected, the receiver lowered and the condenser rinsed with a little hot distilled water.

After adding 5 cc. of concentrated HCl to the distillate, it is concentrated by boiling to approximately 75 cc., using a Bunsen burner. The solution is then filtered into a clean "beaker-flask," the filter and receiver being thoroughly washed with hot distilled water. The filtered solution is then heated to boiling and 10 cc. of BaCl_2 solution slowly added, stirring continuously. The flask is lightly stoppered with a clean cork and allowed to stand over night on a steam bath.

On the following morning the solution is decanted through a 9 cm. blue ribbon ashless filter paper, the precipitate then washed onto the filter and completely removed from the flask with the aid of a rubber tipped rod bent in an angle so as to reach the sides of the flask. The filter is then washed with hot distilled water until the washings are free from chlorides. The filtrate should be perfectly clear and it is advisable to allow the solution to stand on a steam bath for about one hour, when by giving the solution a rotary motion, even traces of precipitate will collect in the center of the flask. If no precipitate appears, the BaSO_4 obtained in the first filtration is ready for ignition; otherwise the solution must be refiltered.

The filter paper, containing the BaSO_4 , is removed from the funnel, at the same time wiping off any trace of precipitate which may have crept over the paper, and it is then placed in a weighed platinum crucible. The paper is ashed, the crucible allowed to cool and the precipitate treated with a drop of pure concentrated H_2SO_4 in order to convert any barium sulfide, which may have been formed by reduction, to BaSO_4 . After expelling the excess of H_2SO_4 , the crucible is heated to a bright red for five minutes, cooled in a desiccator and weighed. The treatment with H_2SO_4 is repeated until a constant weight is obtained. The blank obtained on the reagents is deducted from this weight and the difference gives the percentage of SO_2 in the sample.

NOTE.—27.5 grams of the sample are used, since the weight of BaSO_4 obtained directly gives the percentage of SO_2 without further calculation. It is not necessary to weigh this sample closer than to 0.1 gram.

ORIGIN OF SULFUR DIOXIDE IN GELATIN

I—EFFECT OF DISTILLATION OR POSSIBLE LIBERATION OF VOLATIL SULFUR COMPOUNDS

Alexander,¹ in a paper on the determination of sulfur dioxide in gelatin, considered it likely that some of the organic sulfur in the gelatin is carried over, in the form of volatil sulfur compounds, when distilled with phosphoric acid in a current of CO₂. He also considered it probable that the time and intensity of heating and the concentration of the solution influenced the quantity which appeared in the distillate. This subject has already been discussed in part in connection with steam distillation and direct distillation, but the following experiments have a more direct bearing on the effect of time and intensity of heating:

1. 27.5 grams of gelatin were dissolved in 300 cc. of water and heated in an autoclave at 20 lbs. pressure for 30 minutes. After the addition of phosphoric acid the flask was connected to the distillation apparatus and the amount of SO₂ determined in the usual manner. The result of this determination, expressed in per cent by weight of the original gelatin, was 0.0007 against 0.0013 in the original sample, thus showing a loss of SO₂.

2. Same as Experiment 1, except that the solution was heated for one hour in the autoclave at 20 lbs. pressure. The amount of SO₂ found was 0.0002 per cent, showing a still greater loss of SO₂.

3. Same as Experiment 1, except that the solution was heated for two hours in the autoclave at 20 lbs. pressure. In this experiment 0.0003 per cent of SO₂ was obtained, practically the same amount as found in Experiment 2.

It is evident from these experiments that the heating of the gelatin solution in an unstoppered flask in the autoclave resulted in a loss of SO₂. As the time of heating was increased, the gelatin lost considerably in gelatinizing power and deposited a grayish coagulum. The sample of gelatin selected for this experiment contained an exceptionally small amount of SO₂, the object being to determine whether the heating, in the absence of phosphoric acid, caused a cleavage of the gelatin which would render it more susceptible to attack and possible liberation of volatil sulfur compounds on distillation with phosphoric acid.

4. A fourth experiment was conducted in which 27.5 grams of the same gelatin used in the previous experiments was placed in the distilling flask of the apparatus (Fig. 1), 300 cc. of water added, acidified with phosphoric acid and distilled in the usual manner, collecting 200 cc. of distillate in iodine. By means of a separatory funnel, attached to the distilling flask, 200 cc. of water were added to the residue in the distilling flask, thus replacing the volume of water collected in the distillate: 200 cc. of distillate were again collected in a receiver containing a fresh supply of iodine. This operation was repeated once more, three successive distillates being collected. The amount of SO₂ found in each distillate, expressed in per cent by weight of the original gelatin, was as follows:

Distillate I	= 0.0014%
Distillate II	= 0.0001%
Distillate III	= 0.0000%

This experiment shows that prolonged heating in the presence of phosphoric acid, with the resultant increase in concentration and acidity, does not cause a dissociation of the organic sulfur of the gelatin with

liberation of volatil sulfur compounds which are oxidized to H₂SO₄ by iodine.

The fact that 16 samples, out of over 1000 samples, were found to contain absolutely no SO₂ is convincing evidence that dissociation of the natural sulfur in gelatin, with liberation of volatil sulfur compounds oxidizable to H₂SO₄ by iodine, does not occur under the conditions observed in the determination of SO₂.

It is interesting to note that the only sulfur-containing dissociation-product obtained so far from gelatin¹ by Harbaczewski,¹ is H₂S. Even if this were liberated under the analytical conditions, it would not be oxidized to H₂SO₄ by the iodine solution.

II—SIGNIFICANCE OF SULFUR DIOXIDE IN GELATIN FOR BACTERIOLOGICAL PURPOSES

The fact that the heating of a solution of gelatin under pressure results in a loss of SO₂ is of interest in connection with the preparation of nutrient media for bacteriological work. A sample of sheet gelatin which contained 0.1108 per cent of SO₂ was used to prepare a quantity of nutrient media. Twenty tubes of the preparation, containing in all 26.04 grams of the original gelatin, were analyzed for SO₂ with the following result:

	Found Per cent	Calculated from original SO ₂ content of gelatine Per cent
SO ₂ in nutrient media.....	0.0009	0.0133

The loss in SO₂ which resulted in the process of preparation was, therefore, 93 per cent of the original content of SO₂. Another preparation from the same gelatin contained 0.0006 per cent of SO₂ which corresponds to a loss of 95 per cent. Leffmann and LaWall² have reported the SO₂ content of two samples of imported gelatin, used largely for bacteriological work, as 265 and 835 parts per million and believe that such gelatin is unsuitable for culture medium. They suggest that bacteriologists establish a strict standard for gelatin. The above results on a culture medium prepared from a gelatin containing 1108 parts of SO₂ per million, indicate that this precaution is unnecessary and also account for the fact that bacteriologists have not experienced difficulty when employing media prepared with such gelatin.

III—OCCURRENCE OF SULFUR DIOXIDE IN GELATIN PREPARED FROM RAW MATERIALS FREE FROM SULFUR DIOXIDE

A number of experiments were conducted in which two samples of gelatin were prepared in the laboratory. The bones used for this work were obtained from a calf which was killed in the laboratory in connection with another investigation, so that there was no question as to the origin of the raw material. The bones were carefully freed from adhering meat, chopped into small pieces, thoroughly washed, and 3133 grams were then digested for three days with four times their weight of HCl (sp. gr. 1.15). The material was then washed free from acid, covered with a saturated solution of calcium hydrate and allowed to stand for three

¹ Gustav-Mann, "Chemistry of the Proteids," 1906, p. 562.

² Analyst, 36, 271.

¹ J. Am. Chem. Soc., 29, 783.

days. The material was then thoroughly washed and pressed to remove as much water as possible. The resulting wet "stock" weighed 1580 grams and this was divided in three portions for the following experiments:

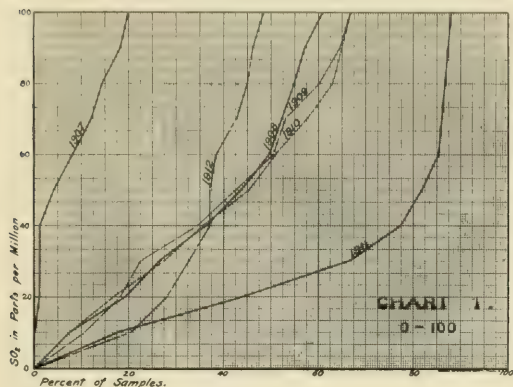
1. The wet "stock" was dried in a current of air and when air-dry it weighed 228 grams, thus showing 57 per cent of water lost from the original to the air-dry condition. A determination of SO_2 on this air-dry material gave 0.006 per cent.

2. The wet "stock" was digested with three times its weight of water for 30 minutes in an autoclave at 22 lbs. pressure, which

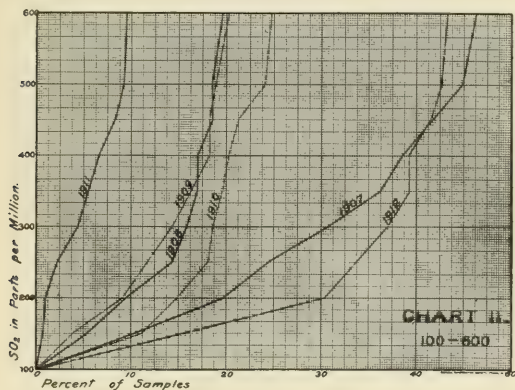
traces of SO_2 which in all probability was also absorbed in the drying. Gas burners were used occasionally in the room where the drying process was carried out and this undoubtedly augmented the SO_2 content. Both products were free from odors of decomposition, so that bacterial influences were not responsible for the rather high SO_2 content.

SULFUR DIOXIDE CONTENT OF COMMERCIAL GELATIN

A large number of samples of commercial gelatin obtained from various sources have been examined

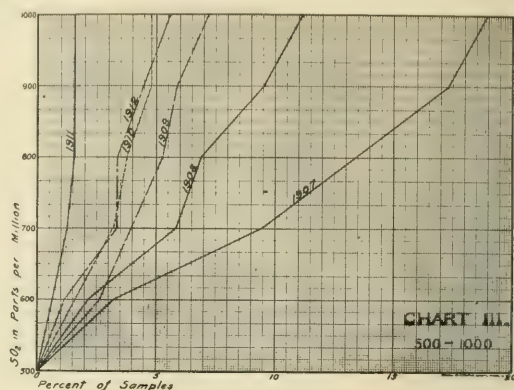


gave a transparent solution. This was poured into a glass tray in which it gelatinized on cooling. This jelly was superficially dried in a current of air from an electric fan and then removed to a wire netting to complete the drying. The entire drying was conducted in a room separated from the main laboratory so as to avoid unusual contamination with sulfurous gases. An analysis of the air-dried product gave 0.0189 per cent of SO_2 .

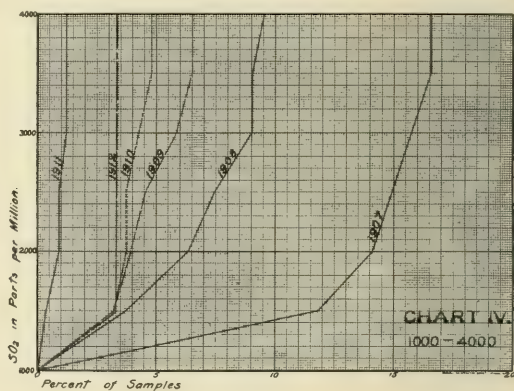


3. This portion was digested with the same amount of water, as in the case of Experiment 2, for 5 hours under reduced pressure, but solution took place so slowly that it was necessary to place the mixture in an autoclave. After 50 minutes' heating at 19 to 22 lbs. pressure, the solution was poured into a tray and then dried as in the case of Experiment 2. An analysis of this product gave 0.0199 per cent of SO_2 .

These experiments show that the SO_2 could only have been absorbed from the air passed over the jelly during the drying. The dry "stock" contained but



in this laboratory. These products include domestic and foreign gelatins and represent the materials produced by more than twenty different manufacturers. From 1907 to 1912 inclusive, 1060 samples were examined. A tabulation of the individual analyses would be unnecessarily burdensome and, therefore, the results have been arranged in groups, expressing



the SO_2 content in parts per million and giving the percentage of samples found within various limits during the years 1907 to 1912 inclusive. Table IV gives the percentage of samples within these limits and Table V gives the same results tabulated in four groups so as to show the total percentage of samples occurring within the limits given for the different groups. In Charts I to IV the data contained in Table V are represented graphically.

TABLE IV
Percentage of samples

SO ₂ Parts per million	1907	1908	1909	1910	1911	1912
0- 10	0.00	7.45	10.45	7.45	17.46	20.22
10- 20	0.78	11.70	7.84	9.09	26.35	7.86
20- 30	0.00	7.45	5.23	10.64	22.85	4.49
30- 40	0.00	9.56	11.11	9.50	10.47	4.49
40- 50	3.15	7.45	7.84	9.56	4.76	0.00
50- 60	3.93	5.85	7.84	5.32	3.17	1.12
60- 70	3.93	2.66	2.62	6.92	0.95	4.49
70- 80	2.36	2.66	7.19	5.32	0.63	2.24
80- 90	3.93	2.12	4.57	2.12	0.63	1.12
90-100	1.57	3.72	1.95	1.60	0.63	2.24
100-150	10.23	5.32	3.90	11.17	0.63	15.73
150-200	9.45	4.25	5.23	3.72	0.31	14.60
200-250	4.72	4.78	2.62	3.20	1.26	3.36
250-300	6.30	1.60	2.62	0.53	2.22	3.36
300-350	5.51	1.06	1.95	1.06	0.95	2.24
350-400	2.36	0.00	1.95	0.53	1.26	0.00
400-450	3.15	1.60	0.00	1.06	1.58	2.24
450-500	3.15	0.00	0.65	2.66	0.95	1.12
500-600	3.15	2.12	2.62	1.60	0.63	1.12
600-700	6.30	3.72	1.31	1.60	0.63	2.24
700-800	3.93	1.06	1.31	0.53	0.31	0.00
800-900	3.93	2.66	0.65	1.06	0.00	1.12
900-1000	1.57	1.60	1.31	0.00	0.00	1.12
1000-1500	11.81	3.72	3.26	3.20	0.31	3.36
1500-2000	2.36	2.66	0.65	0.53	0.63	0.00
2000-2500	0.78	1.06	0.65	0.00	0.00	0.00
2500-3000	0.78	1.60	1.31	0.53	0.31	0.00
3000-3500	0.78	0.00	0.65	0.53	0.00	0.00
3500-4000	0.00	0.52	0.00	0.00	0.00	0.00
Above 4000	0.00	0.00	0.65(a)	0.00	0.00	0.00

(a) Contained 0.7410 per cent, or 7410 parts per million.

TABLE V
Percentage of samples

SO ₂ Parts per million	1907	1908	1909	1910	1911	1912
0- 10	0.00	7.45	10.45	7.45	17.46	20.22
0- 20	0.78	19.15	18.29	16.54	43.81	28.08
0- 30	0.78	26.60	23.52	27.18	66.66	32.57
0- 40	0.78	36.16	34.63	35.62	77.13	37.06
0- 50	3.93	43.61	42.47	45.19	81.89	37.06
0- 60	7.86	49.46	50.31	50.51	85.06	38.18
0- 70	11.79	52.12	52.93	57.43	86.01	42.67
0- 80	14.15	54.78	60.12	62.75	86.64	44.91
0- 90	18.08	56.90	64.69	64.87	87.24	46.03
0-100	19.65	60.62	66.64	66.47	87.90	48.27
100-150	10.23	5.32	3.90	11.17	0.63	15.73
100-200	19.68	9.57	9.13	14.89	0.94	30.33
100-250	24.40	14.35	11.75	18.09	2.20	33.69
100-300	30.70	15.95	14.37	18.62	4.42	37.05
100-350	36.21	17.01	16.32	19.68	5.37	39.29
100-400	38.57	17.01	18.27	20.21	6.63	39.29
100-450	41.72	18.61	18.27	21.27	8.21	41.53
100-500	44.87	18.61	18.92	23.93	9.16	42.65
500-600	3.15	2.12	2.62	1.60	0.63	1.12
500-700	9.45	5.84	3.93	3.20	1.26	3.36
500-800	13.38	6.90	5.24	3.73	1.57	3.36
500-900	17.31	9.56	5.89	4.79	1.57	4.48
500-1000	18.88	11.16	7.20	4.79	1.57	5.60
1000-1500	11.81	3.72	3.26	3.20	0.31	3.36
1000-2000	14.17	6.38	3.91	3.73	0.94	3.36
1000-2500	14.95	7.44	4.56	3.73	0.94	3.36
1000-3000	15.73	9.04	5.87	4.26	1.25	3.36
1000-3500	16.51	9.04	6.52	4.79	1.25	3.36
1000-4000	16.51	9.57	6.52	4.79	1.25	3.36
1000-4000+	16.51	9.57	7.17	4.79	1.25	3.36

The results show that the 1907 samples contained the largest amount of SO₂, only 19.65 per cent of the samples containing less than 100 parts per million and 35.39 per cent above 500 parts per million. The 1908 samples show 60.62 per cent of the samples below 100 parts per million and 20.73 per cent above 500 parts per million. The 1909 and 1910 samples are quite similar throughout. In 1911 the analyses show 87.90 per cent of the samples with less than 100 parts per million and only 2.77 per cent above 500 parts

per million. The 1912 samples contained more SO₂ than the 1911 samples, this being due to the fact that a large number of the 1912 samples, 42.65 per cent, contained from 100 to 500 parts per million.

Comparatively few samples contained less than 10 parts per million. A number of the samples containing less than 10 parts per million were found to contain hydrogen peroxide evidently added to destroy SO₂.

In this connection, the results obtained on the two samples of gelatin prepared in the laboratory are significant. These samples contained 189 and 199 parts per million of SO₂, respectively, whereas the air-dried "stock" from which they were prepared contained only 6 parts per million. Two more samples of gelatin prepared in the laboratory from fresh calf bones, purchased in a butcher shop, contained 23 and 78 parts per million. In this case the jelly was also dried on glass plates in a current of air from an electric fan. It is, therefore, not surprising that even excessive amounts of SO₂ may be found in gelatin prepared from selected stock. In the manufacture of gelatin, the thin gelatin solutions are concentrated to the desired consistency so that gelatinization will take place on cooling. The jelly is then sliced and dried in a continuous current of air at 85 to 95° F. If the factory is situated in a manufacturing district, where much coal is burned, it is to be expected that the SO₂ absorbed by the gelatin would be greater than in the case of gelatin manufactured in outlying districts.

Naturally, the selection of the stock is also important, since it may contain considerable amounts of SO₂. Thirty-six samples of stock examined in 1908, 1909 and 1910 gave the following results:

	Sulfur dioxide Parts per million
Maximum.....	1695
Minimum.....	9
Average.....	407

In conclusion, I wish to acknowledge my indebtedness to my assistant, Mr. E. S. Liebscher, for his painstaking work in carrying out a considerable part of the analyses and experiments.

LEDERLE LABORATORIES
39-41 WEST 38TH STREET
NEW YORK

EXPERIMENTAL DATA ON THE DETERMINATION OF SACCHARIN IN FOODS WITH A MODIFICATION OF SCHMIDT'S METHODS

By HALSEY DURAND
Received October 13, 1913

A recent ruling of the Board of Health of the Department of Health of New York City prohibited the use of saccharin in foods and drinks (see Section 68, Sanitary Code). The enforcement of this law required the examination of a large number of samples of various foodstuffs and soft drinks in which violations were expected.

A method for the detection of saccharin was sought which could be done positively and with as much speed as possible.

A review of the literature gave five methods, as follows:

I. TASTE TEST. The aqueous solution of the sample is acidified and shaken out with ether. The ethereal layer separated and evaporated to dryness and a small portion of the residue applied to the tongue. An extremely sweet taste followed by a bitter taste indicates saccharin.

II. BORNSTEIN'S TEST.—(*Z. anal. Chem.*, **27**, s. 165). Aqueous solution is shaken as above and the ether residue heated with resorcin and a few drops of concentrated sulfuric acid, till the mass begins to swell. Cool. Repeat heating and cooling several times. Cool, dilute with water and neutralize with sodium hydrate. Red-green fluorescence indicates presence of saccharin.

III. KASTLE'S TEST.—(*Bull.* **26**, Hyg. Lab., U. S. Pub. Health & Mar. Hosp. Serv.) The ether residue is treated with a few drops of a mixture of 5 cc. of phenol and 3 cc. of pure concentrated sulfuric acid. It is then heated for 5 minutes to 160–170° C. and the mass dissolved in water and made alkaline with sodium hydrate. A dark purplish red or pink indicates the presence of saccharin.

IV. SCHMIDT'S TEST.—(*Rep. Anal. Chem.*, **30**.) Residue from ether extraction is heated in a porcelain dish with about 1 gram sodium hydrate for one-half hour at 250° C. in air oven or linseed oil bath. This converts saccharin to sodium salicylate. The melt is dissolved in water, acidified with hydrochloric acid and shaken with ether. Evaporate ether, take up residue with water and add dilute ferric chloride solution. A violet color indicates the presence of saccharin. The absence of salicylic acid must first be ascertained before applying this method. If salicylic acid is present the ether residue is treated with dilute hydrochloric acid and bromine water added in excess. The liquid is well shaken and filtered. The salicylic acid is completely removed as a bromine derivative. The filtrate is made strongly alkaline and evaporated and heated as above. By this means the false saccharin frequently found in wines and giving faint reactions for saccharin is also eliminated.

V. ALLEN'S TEST.—(*Allen's Com. Organ. Anal.*, **2**, Pt. 3, p. 38.) The ether residue is rendered alkaline with sodium hydrate and ashed. The ash is taken up with water made acid with hydrochloric acid and tested with barium chloride or sulfur. The presence of sulfur indicates saccharin.

This test, a little potassium nitrate being added during ignition, is also used for the quantitative determination of saccharin, the barium sulfate being weighed and the weight $\times 0.783$ = saccharin. This quantitative method was not tried as the presence of saccharin is sufficient ground for prosecution.

TEST I.—The taste test was tried and found to be very satisfactory, the absence of the sweet taste being a good indication in most cases of the absence of saccharin. However, the possibility of other substances producing the sweet taste, and also of the sweet taste being masked by bitter substances in the residue, made it necessary to have some further test as confirmation.

TEST II was tried and gave good reactions. It

was found, however, that a large number of organic compounds give the same reaction as saccharin, so this method was discarded.

TEST III was tried and excellent results were obtained when pure saccharin was used. When ether residues obtained from shaking out aqueous solutions of foods and drinks were treated with the phenol-sulfuric acid mixture and neutralized with sodium hydrate the characteristic color did not appear. The failure of this reaction is evidently due to the presence of small amounts of impurity in the residue. Efforts were made to obtain the pure phenol compound from the aqueous solution after treating the residue with phenol-sulfuric acid mixture, by shaking out with amyl alcohol and isobutyl alcohol and treating the separated alcohol solutions with sodium hydrate, without results.

TEST IV (Schmidt's) was tried repeatedly by the laboratory force using the various modifications as suggested by different authorities. Invariably the ether residue, obtained by shaking out the acidified aqueous solution of the mass after heating, gave a benzoic acid reaction on addition of dilute ferric chloride solution. It was found also that the saccharin in the original ether residue was converted into benzoic acid when treated with saturated sodium hydrate solution and allowed to stand over night at room temperature. Excellent results were obtained in this way and this method was adopted by this laboratory as a confirmatory test to be used with the taste test. This method while giving good results required too long a time for its completion.

METHOD ADOPTED

The writer has recently succeeded in obtaining the salicylic acid by Schmidt's method (IV) both in pure saccharin and in ether residues containing saccharin, by proceeding as follows:

One hundred cc. of an aqueous solution of the sample to be examined for saccharin are acidified with phosphoric acid and shaken out with ether in the usual manner. The separated ether is filtered through double folded filter papers, to remove moisture, into a nickel dish of convenient size and evaporated to dryness. After ascertaining the absence of salicylic, (see description of Schmidt's method), the residue is treated with about 1 cc. of saturated sodium hydrate solution, allowing the alkali to come in contact with the entire residue. Place the dish on a piece of asbestos board about 3 mm. in thickness, heat for 8–10 minutes over a Bunsen flame, cool, take up with water, acidify with hydrochloric acid, and shake out with ether. Evaporate ether, to which a small amount of ammonium hydrate has been added, in a glass dish on water bath, take up residue with a little water and test with dilute ferric chloride for salicylic acid. This method gave very satisfactory results requiring about three-quarters of an hour.

The writer has further simplified and shortened the time required for the method and also eliminated the possibility of the sublimation of the salicylic acid on the water bath by omitting the treatment of the final ether residue with ammonium

hydrate and its evaporation to dryness. The ether residue, after separation, is poured into a test tube and about 5 cm. of water containing a small amount of ferric chloride are added. The test tube is then shaken vigorously and the ether and water layers allowed to separate. The presence of salicylic acid is indicated by a violet coloration of the water layer.

CHEMICAL LABORATORY, DEPARTMENT OF HEALTH
NEW YORK CITY

BOUILLON CUBES

By F. C. COOK¹

Received September 13, 1913

INTRODUCTION

Bouillon cubes consist of a large amount of common salt mixed with varying amounts of meat and plant extract, a small per cent of fat, and a little condiment. Some of the products sold under the name "bouillon cubes" contain but a small per cent of meat stock or extractives, and are not entitled to the term "bouillon" unless it is modified. They are extensively advertised as capable of making a stimulating and appetizing hot drink simply by being dissolved in hot water. They have, therefore, a legitimate place among our dietary accessories.

Several brands of these cubes have appeared on the

of the Association of Official Agricultural Chemists,¹ total creatinin by the Benedict-Myers² autoclave method, and precipitation with alcohol in hydrochloric acid solution was carried out according to Rippeteo's method,³ which is as follows:

Rippeteo's Method.—Transfer 10 cc. of an aqueous solution containing 2 grams of the sample to a 200 cc. glass-stoppered measuring cylinder, add 1.2 cc. of 12 per cent hydrochloric acid, mix and add absolute alcohol to the 200 cc. mark, shake and let stand several hours at 20 to 25° C. If necessary make to mark, filter, and determine total nitrogen in 100 cc. of filtrate.

The acidity figures were obtained by titrating one gram of the sample dissolved in 100 cc. of water with twentieth-normal sodium hydroxide, using phenolphthalein as indicator. The results obtained on the ten samples of cubes analyzed are given in Tables I and II.

The water content of the cubes examined was under 5 per cent and the ether extract figures varied from 1 to 4.58 per cent. These last figures represent the amount of fat added to these cubes during the process of manufacture. The ash, which is largely sodium chloride, varied from 50 to 74 per cent. A large amount of sodium chloride is necessary to give a salty taste to the cup of water in which the cube is dissolved, and

TABLE I—ANALYSIS OF BOUILLON CUBES—ORIGINAL BASIS

Sample No.	Brand	Solids Per cent	Organic material Per cent	Ether extract Per cent	Ash Per cent	Total chlorine as sodium chloride Per cent	Total phosphoric acid (P ₂ O ₅) Per cent	Acidity (cc. twentieth-normal sodium hydroxid per 1 gram)	Total nitrogen Per cent	Nitrogen precipitated by absolute alcohol in hydrochloric acid Per cent	Total creatinin Per cent
1977	Behrend	96.60	22.86	1.93	73.74	72.13	1.02	6.20	2.19	0.13	0.84
1978	Oxo	95.06	25.31	3.10	69.75	65.00	1.51	6.50	2.97	0.86	1.07
1979	Stereo	96.05	28.41	1.20	67.64	62.15	1.83	9.15	3.62	0.76	1.67
1980	Burnham	96.87	41.94	1.00	54.93	52.90	0.58	6.10	2.11	0.05	0.88
1981	Sunbeam	95.73	45.23	1.44	50.50	49.26	0.54	7.30	2.36	0.02	0.92
1982	Armour	96.05	26.48	0.96	69.57	67.44	0.62	6.00	2.79	0.17	1.07
1983	Morris	96.77	33.00	3.79	63.77	59.17	1.69	9.68	3.67	0.56	1.07
1984	Standard	95.81	21.76	4.19	74.05	72.22	0.48	5.01	2.09	0.07	0.50
1985	Liggitt	96.00	21.91	4.58	74.09	71.98	0.41	4.75	2.11	0.05	0.49
1986	Knorr	95.44	26.24	4.57	69.20	65.00	1.55	7.40	3.20	0.91	1.38

American market in the past five years, most of them manufactured in this country, and some imported from Germany. Many are wrapped in tin foil, while others are wrapped in paraffin paper, and occasionally a brand of cubes is found in both foil and paper. As the moisture content is low and a large amount of salt is present, they will keep indefinitely, although certain makes tend to lose their form during warm weather.

The bouillon cubes which are reported in this paper were collected on the New York market in 1912.

METHODS OF ANALYSIS

The samples were prepared for analysis by grinding fifteen to twenty cubes in a mortar as thoroughly as possible and placing the composite paste in small screw-cap jars. The solids were obtained by drying to constant weight *in vacuo* at 65° C. The ash, sodium chloride, phosphoric acid (P₂O₅), nitrogen, and ether extract were determined by the methods

¹ Physiological Chemist, Animal Physiological Chemistry Laboratory, Bureau of Chemistry.

to furnish body to the cube. Sudendorf⁴ analyzed 18 samples of cubes bought on the market at Hamburg, Germany, and two samples prepared in his

TABLE II—ANALYSIS OF BOUILLON CUBES—WATER, FAT, AND ASH-FREE BASIS

Sample No.	Brand	Phosphoric acid (P ₂ O ₅) Per cent	Total nitrogen Per cent	Total creatinin Per cent	Ratio of creatinin to total nitrogen
1977	Behrend	4.86	10.50	4.01	1 : 2.6
1978	Oxo	6.80	13.37	4.82	1 : 2.8
1979	Stereo	6.73	13.30	6.14	1 : 2.2
1980	Burnham	1.41	5.03	2.10	1 : 2.4
1981	Sunbeam	1.23	5.39	2.10	1 : 2.6
1982	Armour	2.43	10.94	4.19	1 : 2.6
1983	Morris	5.78	12.57	5.82	1 : 2.2
1984	Standard	2.73	11.88	2.84	1 : 4.2
1985	Liggitt	2.37	12.18	2.83	1 : 4.3
1986	Knorr	7.14	14.75	6.36	1 : 2.3

laboratory. The latter contained sufficient salt to give a satisfactory taste to the cup of bouillon. The

¹ Bull. 107, Rev., Bureau of Chemistry, U. S. Dept. Agr.

² Am. J. Phys., 18, 397 (1907).

³ Private communication.

⁴ Z. Nahr. Genussm., 23, 577 (1912).

results showed that 65 per cent of sodium chloride is sufficient to be added to a cube.

The figures for total creatinin vary according to the amount and kind of the meat extract present. The total creatinin includes the original creatinin of the cube and the creatin which has been changed to creatinin in the autoclave. As both substances are structurally closely related, and have a common origin in the creatin of the muscle, only the figure for total creatinin is given in this table. The determination of creatinin is very important in this work as it is of value in showing how much meat extract was used in preparing the cube. According to Seiger,¹ if we place the creatinin content of meat extract at 6 per cent, then bouillon cubes should contain the following amounts of creatinin:

Meat extract used Per cent	Creatinin contained Per cent
25	1.5
20	1.2
15	0.9
10	0.6

The creatinin determination is applied to the water solution of the cube or meat extract. As noted² by the writer before, there is not sufficient protein present in ordinary meat extract to interfere with the creatinin test. Geret³ has recently stated that the meat extract content of different cubes, based on the analyses of Liebig's meat extract, varies from 20 to 25 per cent for the superior cubes while the inferior cubes contain no creatinin. He also stated that gelatin increases the creatinin results. In a previous publication the writer stated that egg albumen and Witte's peptone, when added to solutions containing creatinin, decreased the creatinin result. The figures on which these statements are based were obtained by the Benedict-Myers method. It is likely that solutions of creatin containing gelatin or egg albumen, when evaporated to dryness or otherwise treated, would give high creatinin figures due to caramel or other colored products formed during the process, which might account for the high figures obtained by Geret.

Meat extract contains a higher per cent of total nitrogen than plant extract; therefore, a cube prepared largely from meat extract has a higher total nitrogen content than one prepared largely from plant extract. A good cube is indicated by high creatinin and high nitrogen figures. The results obtained by precipitation with absolute alcohol in hydrochloric acid solution, as outlined above, show that a larger per cent of nitrogen is precipitated in a high-grade than in a low-grade cube, and the figures are of some value in determining how much meat extract has been used in the preparation of the cube. The nitrogen precipitated by absolute alcohol in hydrochloric acid is not appreciably affected by the sodium chloride present. The acidity figures are of little value in determining the nature of the constituents present in a bouillon cube.

The phosphoric acid (P_2O_5) results, especially when calculated to a water, fat, and ash-free basis, show higher figures for the superior cubes than for the inferior ones. The value of the phosphoric acid (P_2O_5), total nitrogen and total creatinin results are more apparent on the water, fat, and ash-free basis than on the original basis. The creatinin-total nitrogen ratios show little in regard to the composition of the cubes, as a low creatinin figure due to the use of a small amount of meat extract, and a low total nitrogen figure due to the use of a large amount of plant extract would be found in the same product. From a survey of Sudendorf's analyses of cubes collected on the German market it is apparent that the cubes sold on the market in this country are very similar in composition to those on the German market, that is, both consist of a large amount of salt, together with smaller amounts of meat and plant extracts.

SUMMARY

Bouillon cubes on the market at present consist of about 5 per cent of water, 1 to 4.5 per cent of ether extract (fat), and 50 to 74 per cent of ash which is practically all sodium chloride. The nitrogen bodies and undetermined organic material amount to 20 to 40 per cent. The phosphoric acid (P_2O_5) varies from 0.4 to 1.8 per cent, the total nitrogen from 2.1 to 3.6 per cent, and the total creatinin from 0.49 to 1.67 per cent.

A cube prepared largely from meat extract gives high total phosphoric acid (P_2O_5), total nitrogen, and total creatinin figures. The amount of nitrogen precipitated by absolute alcohol and hydrochloric acid is also markedly higher than in a cube containing much plant and little meat extract.

Bouillon cubes are extensively advertised and are sold on account of their flavoring and stimulating properties, rather than for any slight food value they may possess. The large per cent of sodium chloride, which need not exceed 65 per cent, is used to furnish body to the cube and to give a salty taste to the cup of water in which the cube is dissolved.

Bouillon is a clear broth, the basis of which is meat; consequently a true bouillon cube should show high creatinin and high total nitrogen figures, and should be prepared entirely, or largely from meat stock or meat extract in addition to the salt and fat present. Several of the cubes on the market contain much more plant than meat extract and are not entitled to the name "bouillon" unless modified.

BUREAU OF CHEMISTRY
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

THE INFLUENCE OF BRAN-EXTRACTS ON THE BAKING QUALITIES OF FLOUR

By H. L. WHITE

Received September 6, 1913

It is generally recognized that bran and shorts contain valuable food constituents such as fat, carbohydrates other than cellulose, mineral matter and some nitrogenous material. Attempts have been made to improve the bread-making qualities of a flour, by in-

¹ *Konserven Ztg.*, **48**, 378 (1912).

² *J. Am. Chem. Soc.*, **31**, 673 (1909).

³ *Z. Nahr. Genussm.*, **24**, 570 (1912).

roducing into the flour extracts of bran made with various solvents. Thus cold water extracts and hot water extracts¹ have been mixed with flour in varying proportions with beneficial results. A process has been patented² for treating bran in order to recover the mineral constituents for admixture with flour. The bran is treated with water to extract soluble salts and the residue treated with an acid solvent and water and subsequently with an alkaline solution. The acid and alkali solutions are neutralized, and the whole of the extracts are evaporated to dryness, and the residue is reduced to a powder.

In connection with some experimental work on the mineral content of flour, it was found advisable to determine the effect of a dilute hydrochloric acid-extract of bran on the baking qualities of flour made from several varieties of wheat. It has been claimed³ that a 0.2 per cent HCl extract of bran contains phytin from which an acid identical with Posternak's⁴ anhydrooxymethylen diphosphoric acid is obtained. That phytin is obtained in this manner is denied by Anderson⁵ who claims that the extract thus obtained does not correspond in composition with salts of the true phytic acid. Without entering into the discussion of this point, the fact remains that the dilute acid extract contains, in addition to other constituents, both organic and inorganic phosphorous compounds.

EXPERIMENTAL

The acid-extract used in these experiments was prepared by soaking bran in 0.2 per cent HCl for sixteen hours. The proportions used were, bran 300 grams, acid 1800 cc. The liquid was first filtered through cheese-cloth and then through paper, a clear liquid of a brown color being thus obtained. Analysis of this clear liquid gave the following results:

TABLE I—COMPOSITION OF ACID-EXTRACT OF BRAN

Total Solids	Ash	Total	Inorganic	Organic	Acidity
Grams	Grams	P ₂ O ₅	P ₂ O ₅	P ₂ O ₅	cc. N/20
per 100 cc.	per 100 cc.	per 100 cc.	per 100 cc.	per 100 cc.	per 10 cc. ext.
3.584	0.917	0.464	0.200	0.264	13.6

In one series of baking tests the acid-extract was neutralized with 0.1 N NaOH, using phenolphthalein as an indicator. In another series a water-extract (bran 300 grams, water 1800 cc.) was used, and in still another, 0.2 per cent HCl was used in place of a bran extract. A comparison of these various extracts is afforded in the following table:

TABLE II—COMPOSITION OF VARIOUS EXTRACTS USED IN BAKING TESTS

	Total solids	Ash	Total	Inorganic	Organic	Acidity
	Grams	Grams	P ₂ O ₅	P ₂ O ₅	P ₂ O ₅	cc. N/20
	per 100 cc.	per 100 cc.	per 100 cc.	per 100 cc.	per 100 cc.	NaOH for 10 cc. ext.
Acid-extract.....	3.584	0.917	0.464	0.200	0.264	13.6
Water-extract.....	2.776	0.444	0.163	0.110	0.053	3.0
Acid-extract, neutralized.....	3.785	1.145
0.2% HCl.....	10.65

¹ Willard and Swanson, *Chem. News*, **105**, 97-9.

² U. S. Patent, No. 1,018,441.

³ Patten and Hart, New York Exp. Sta., *Bull.* **250**.

⁴ Posternak, *Compt. rend.*, **137**, 439.

⁵ Anderson, New York Agric. Exp. Sta., *Technical Bull.* **22** (1912).

BAKING TESTS

Several series of baking tests were made, some months apart, using flour made from the same samples of wheat but freshly ground for each series of tests. In Series I (spring of 1912) varying amounts of extract were used, while in Series II (fall of 1912) the same amount (150 cc.) was used in every case. The bread was made in the usual way, the extracts being used instead of water to make the dough. Straight flours from each of three varieties of wheat were used in these experiments: Bluestem (Lab. No. 568), Durum (Lab. No. 481), and Velvet Chaff (Lab. No. 993).

TABLE III—RESULTS OF BAKING TESTS—SERIES I—BLUESTEM WHEAT
Acid-Extract

1st Baking	Extract	Water	Volume loaf	Color	Texture
	Cc.	Cc.	Cc.		
568A (check).....	..	201	2460	95	96
568B.....	80	123	2760	97	98
568C.....	150	52	2820	100	100
568D.....	150	50	3020	100	100
2nd Baking	Acid-Extract				
568A (check).....	..	200	2460	95	96
568E.....	80	120	2850	97	98
568F.....	170	30	2920	98	100
3rd Baking	Acid-Extract Neutralized ("Soapy")				
568A (check).....	..	196	2640
568G.....	80	122	2590
568H.....	170	36	2280
4th Baking	Dilute Hydrochloric Acid (0.2%)				
568A (check).....	..	205	2690	99	98
568I.....	80	121	2680	101	98
568J.....	140	65	2700	99	97

In both the first and second bakings using acid-extract there was an increase in volume, amounting to 18 per cent, and an improvement in both color and texture. With the neutralized acid-extract there was a decrease in loaf volume amounting to 13 per cent.

In order to determine if the use of acid-extract resulted in an increase of acid-reacting material in the bread, the soft portions of loaves, Nos. 568A (check) and 568D (150 cc. extract) were extracted with water and the filtered solution titrated with 0.05 normal NaOH, with the following results:

TABLE IV—ACIDITY OF INNER PORTIONS OF LOAVES OF BREAD

Lab. No.	N/20 NaOH	Calculated as lactic acid	Calculated as HCl
	Cc.	Per cent	Per cent
568A (check).....	4.3	0.193	0.078
568D (extract).....	8.35	0.373	0.152

The average acidity of the inner portion of twenty-one samples of fresh bread was found¹ to be equivalent on a dry basis to 0.289 per cent lactic acid or 0.215 per cent hydrochloric acid. Therefore, the acidity of the water-soluble portions of 568A and 568D is about the same as the average of home-made bread and of bakers' bread.

TABLE V—SERIES I—DURUM WHEAT
Acid-Extract

1st Baking	Extract	Water	Volume loaf	Color	Texture
	Cc.	Cc.	Cc.		
481A (check).....	..	190	2040	97	94
481B.....	80	107	2090	97	95
481C.....	140	51	2170	97	96

¹ Congdon, Twenty-second Annual Report, North Dakota Agricultural Experiment Station, **1911**, Part II.

This flour did not respond to treatment with acid-extract as the gain in loaf volume was only 5 per cent, color and texture remaining about the same in each loaf.

TABLE VI—SERIES I—VELVET CHAFF WHEAT

1st Baking	Acid-Extract				
	Extract Ce.	Water Ce.	Volume loaf Ce.	Color	Texture
993A (check).....		190	1980	96	92
993B..... 80		110	2260	99	96
993C..... 160		30	2400	98	96
2nd Baking	Acid-Extract				
	Extract Ce.	Water Ce.	Volume loaf Ce.	Color	Texture
993A (check).....		187	2090	96	95
993D..... 80		108	2340	97	98
993E..... 150		38	2380	98	98
3rd Baking	Acid-Extract, Neutralized				
	Extract Ce.	Water Ce.	Volume loaf Ce.	Color	Texture
993A (check).....		190	2200	100	93
993F..... 80		113	2090	99	92
993G..... 140		55	1970	99	90
4th Baking	Dilute Hydrochloric Acid (0.2%)				
	Extract Ce.	Water Ce.	Volume loaf Ce.	Color	Texture
993A (check).....		187	2090	96	95
993H..... 80		108	2230	97	95
993I..... 150		38	1910	94	85

As shown in the above table there was an increase in the loaf volume of from 13 per cent to 21 per cent when acid-extract was used, and both color and texture were improved. With neutralized extract there was a decrease in loaf volume. With dilute acid alone there was a decrease of 9 per cent in loaf volume, a slight change in color, and a poor texture.



PLATE I
1. Check loaf 4. Acid-extract
2. Water-extract 5. Acid alone
3. Acid-extract, neutralized

After a study of these results, it was decided to make a second series of baking tests, including in each baking all of the extracts which had been used in the several bakings of Series I and in addition a filtered cold-water-extract of bran.

TABLE VII—SERIES II—BLUESTEM WHEAT—No. 568

Flour No. 568	Extract				
	Extract Ce.	Water Ce.	Volume loaf Ce.	Color	Texture
Check.....		190	2490	94	97
Check.....		189	2480	95	97
Acid-extract.... 150		40	2600	96	98
Acid-extract.... 150		40	2690	96	98
Water-extract... 150		40	2600	92	98
Water-extract... 150		39	2515	93	97
Acid-ext., neutral 150		39	2240	94	92
Acid-ext., neutral 150		49	2360	92	92
Dilute acid..... 150		39	2250	94	90
Dilute acid..... 150		40	2200	94	90

A consideration of data submitted in Table VII shows that the acid-extract and water-extract gave somewhat larger loaves than the check, in the order named; and that with the acid-extract both color and texture were slightly improved. Plate I gives some idea of the external appearance of the loaves.

TABLE VIII—SERIES II—DURUM WHEAT

Flour No. 481	Extract				
	Extract Ce.	Water Ce.	Volume loaf Ce.	Color	Texture
Check.....		200	1920	96	95
Check.....		199	1870	96	95
Acid-extract.... 150		48	2030*	96	94
Acid-extract.... 150		51	1870*	96	98
Water-extract... 150		50	2010	95	96
Water-extract... 150		51	2030	95	96
Acid ext., neutral 150		51	1910	97	96
Acid ext., neutral 150		51
Dilute acid..... 150		50	1630	94	85
Dilute acid..... 150		50	1650	94	85

* Baker's comment: "Dough broke slightly."

A consideration of the data submitted in Table VIII indicates but little improvement in loaf volume, color, or texture by the use of acid-extract. The water-

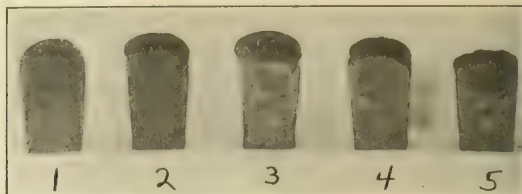


PLATE II
1. Check loaf 4. Acid-extract, neutralized
2. Water-extract 5. Acid alone
3. Acid-extract

extract gave better results than the acid-extract. The dilute acid decreases loaf volume and unfavorably modifies the texture.

TABLE IX—SERIES II—VELVET CHAFF WHEAT

Flour No. 993	Extract				
	Extract Ce.	Water Ce.	Volume loaf Ce.	Color	Texture
Check.....		188	2030	95	95
Check.....		187	2060	95	95
Acid-extract.... 150		36	2480	98	97
Acid-extract.... 150		36	2460	98	97
Water-extract... 150		36	2340	94	96
Water-extract... 150		34	2200	94	96
Acid-ext., neutral 150		35	2020	95	95
Acid-ext., neutral 150		36	2040	95	95
Dilute acid..... 150		36	1870	92	80
Dilute acid..... 150		36	1700	92	80

As will be noted in Table IX, the acid-extract exerted a favorable influence on the baking qualities of flour from velvet chaff wheat, increasing the loaf volume, and giving a better color and texture. The

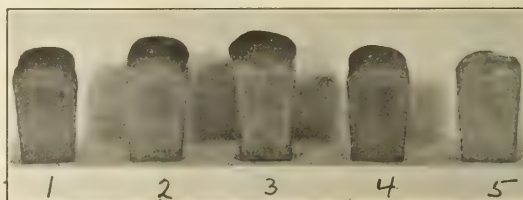


PLATE III
1. Check loaf 4. Acid-extract, neutralized
2. Water-extract 5. Acid alone
3. Acid-extract

water-extract increased loaf volume, but had little influence on color and texture. The dilute acid on the other hand had a marked unfavorable influence on

loaf volume and texture, and, to a lesser degree, the color.

In view of the fact that in the larger number of baking tests the acid-extract had a greater influence than the water-extract to increase loaf volume and to improve the color and texture, the question naturally arises as to whether the improvement is due to the stimulating effect of acid, or phosphate, or other constituent of the extract on the yeast; or to some other factor. Experiments undertaken to determine the stimulating effect of acid-extract on yeast were not convincing. A possible explanation is that the gluten may have become more coherent in the presence of acid and soluble salts (particularly phosphates) as is suggested by Wood.¹ At any rate, the baking tests show clearly that it is not acid alone, but acid plus extractive material that gives the best results.

SUMMARY AND CONCLUSIONS

In two series of baking tests of flour made from three varieties of wheat, acid-extract of bran, water-extract, acid-extract neutralized, and dilute acid, were used to replace a part of the water necessary to make the dough.

In general, the acid-extract produced larger loaves of bread (from 6 per cent to 20 per cent increase in volume) of a better color and texture than the check loaf, or those in which other extracts were used. The water-extract produced loaves somewhat larger than the check loaves. The dilute acid gave a loaf of decreased volume and very poor texture.

Analyses of acid- and water-extracts show the presence of 0.464 gram P_2O_5 and 0.163 gram P_2O_5 , respectively, in 100 cc. extract.

Experiments made to show the stimulating effect of acid-extract on yeast were not convincing. It is thought the presence of both acid and soluble salts makes the gluten more coherent.

In general the better the flour, that is the stronger the gluten, the more marked is the improvement by use of acid-extract; but all samples of flour show greater or lesser improvement.

The inner portions of the loaves of bread made with acid-extract show no greater amount of water-soluble acid reacting material than the average of home-made, or bakers' bread.

In conclusion, the writer wishes to acknowledge his indebtedness to L. M. Thomas, of the Division of Grain Standardization, Bureau of Plant Industry, U. S. Dept. of Agriculture, for his cooperation in making the baking tests, scoring the bread and for making the photographs that are used in this report.

NORTH DAKOTA AGRICULTURAL COLLEGE

THE ANALYSIS OF MAPLE PRODUCTS, II A Comparative Study of the Delicacy of Methods²

By J. F. SNELL AND J. M. SCOTT

In studying the usefulness of the electrical conductivity test³ for the detection of adulteration in maple syrup it appeared desirable to compare the delicacy

¹ T. B. Wood, *Jour. Agr. Sci.*, **2**, 267 (1907); Abstract in *J. Soc. Chem. Ind.*, **27**, 175 (1908).

² Paper presented at the 48th Meeting of the A. C. S., Rochester, September 8-12, 1913.

³ Snell, *This Journal*, **5**, 740 (1913).

of this test with that of other methods in vogue. For this purpose three syrups, A, B, and C, were chosen. A, a light-colored syrup of high quality, and B, a mixture of several pure maple syrups, were kindly donated by Mr. John H. Grimm, of Montreal, while C was a syrup made at Macdonald College in the season of 1913.

These were diluted with water and boiled to 219° F., after which their specific gravities at 60° F. were: A, 1.325; B, 1.320; C, 1.318. Cane-sugar syrups of the same specific gravities were prepared from granulated sugar and mixtures of the cane and maple syrups made up and analyzed.

The following determinations were made upon each of the mixtures:

- (1) Total ash by ignition in an electric muffle at a low red heat (600-650° C.).
- (2) Insoluble ash.¹
- (3) Soluble ash by difference.
- (4) Alkalinity of insoluble ash.¹
- (5) Alkalinity of soluble ash.¹
- (6) Conductivity value, *i. e.*, 100,000 times the specific conductivity at 25° C. of a mixture of one volume syrup with two volumes of water.²
- (7) Canadian lead number.³
- (8) Winton lead number. In Syrups B and C this determination was made upon 25 grams of syrup as originally directed by Winton,⁴ the blank being treated with acetic acid as directed by Bryan.⁵

In Syrup A, however, the determination was made upon the quantity of syrup (38.462 grams) containing 25 grams of dry matter, the procedure prescribed by the Canadian standard of purity for maple syrup.⁶

- (9) Ross's modified Winton number.⁷

This determination also was made on 25 grams of syrup in Syrups B and C, but upon 38.462 grams in syrup A.

- (10) Sy lead value.⁸ Weight of lead precipitated from normal lead acetate by 100 cc. of syrup.

The results obtained are shown in Tables I, II, and III. In Tables IV, V, and VI the actual percentage of maple syrup in each mixture is compared with the "estimated percentages" derived from the ratios of the various values in the mixture to those in the pure syrup.

EFFECTS PRODUCED UPON THE VARIOUS DATA BY PROGRESSIVE DILUTION WITH SUCROSE SYRUP

It will be noted that the ratios of the weights and also those of the alkalinities of the soluble ash to the insoluble ash remain nearly constant down to the 50 per cent mixture. In mixtures containing less than 50 per cent. of maple syrup, these ratios fluctuate greatly. These fluctuations are doubtless due to the

¹ Jones, Vermont Agr. Expt. Sta., 18th Ann. Rept., 1904-5, 321; Bryan Bur. Chem., U. S. Dept. Agr., Bull. **134**, 17 (1910); McGill, Lab. Inland Revenue Dept., Ottawa, Bull. **228**, 5 (1911).

² Snell, *loc. cit.*

³ McGill, *loc. cit.*

⁴ Winton and Kreider, *J. Am. Chem. Soc.*, **28**, 1204 (1906).

⁵ Bryan, *loc. cit.*

⁶ Canadian Order-in-Council, G, 994, Nov. 8, 1911; McGill, Lab. Inland Rev. Dept., Bull. **228**, 5 (1911).

⁷ Ross, Bur. Chem., U. S. Dept. Agr., Circ. **53**, 8 (1910).

⁸ Sy, *J. Frank. Inst.*, Dec., 1908, page 68 of reprint.

TABLE I—MAPLE SYRUP A

Per cent maple syrup	Per cent total ash	Per cent insoluble ash	Per cent water sol ash	Sol. ash: Insol. ash	Alkalinity insol. ash	Alkalinity sol. ash	Alk. sol. ash: Alk. insol. ash	Conductivity value	Canadian lead number	Modified Winton* lead no.	Modified Ross* lead no.	Sy lead value
100	1.14	0.48	0.69	1.53	86	47	0.84	136	2.26	1.46	1.78	0.342
90	1.08	0.38	0.70	1.89	84	53	0.96	136	1.71	1.44	1.69	0.399
80	0.86	0.38	0.51	1.46	46	42	0.91	115	1.58	1.23	1.60	0.273
70	0.68	0.26	0.42	1.62	38	36	0.92	101	1.38	1.18	1.50	0.229
60	0.73	0.28	0.46	1.84	36	31	0.86	90	1.10	1.04	1.39	0.194
50	0.68	0.20	0.48	2.40	31	26	0.84	78	0.70	0.72	1.33	0.179
40	0.32	0.14	0.18	1.29	20	20	1.00	65	0.36	0.55	1.23	0.104
30	0.20	0.14	0.06	0.43	22	12	0.55	50	0.14	0.30	1.04	0.075
20	0.15	0.06	0.09	1.50	16	14	0.87	35	turbidity only	0.16	0.80	0.052
10	0.09	0.02	0.07	3.50	10	4	0.40	20	faint turbidity	0.00	0.44	0.020

* Winton and Ross methods on 25 grams dry sugar = 38.462 grams syrup.

TABLE II—MAPLE SYRUP B

Per cent maple syrup	Per cent total ash	Per cent insoluble ash	Per cent water sol ash	Sol. ash: Insol. ash	Alkalinity insol. ash	Alkalinity sol. ash	Alk. sol. ash: Alk. insol. ash	Conductivity value	Canadian lead number	Winton* lead number	Ross* lead number	Sy lead value
100	0.92	0.40	0.52	1.30	65	52	0.80	170	3.18	1.46	1.72	0.460
90	0.80	0.37	0.43	1.16	62	48	0.77	147	2.67	1.34	1.64	0.378
80	0.71	0.25	0.46	1.84	57	41	0.72	144	2.12	1.19	1.48	0.296
70	0.62	0.26	0.36	1.38	52	38	0.73	126	1.81	1.03	1.34	0.259
60	0.55	0.22	0.33	1.50	46	31	0.67	109	1.60	0.89	1.16	0.239
50	0.49	0.20	0.29	1.45	38	28	0.74	95	1.06	0.73	1.08	0.177
40	0.38	0.12	0.26	2.17	26	26	1.00	77	0.74	0.54	0.82	0.128
30	0.32	0.09	0.23	2.56	19	23	1.21	58	0.31	0.38	0.66	0.074
20	0.22	0.06	0.16	2.67	12	14	1.17	47	turbidity only	0.23	0.37	0.050
10	0.08	0.02	0.06	3.00	10	9	0.90	24	no turbidity	0.11	0.10	0.022

* Winton and Ross methods on 25 grams syrup.

TABLE III—MAPLE SYRUP C

Per cent maple syrup	Per cent total ash	Per cent insol. ash	Per cent water sol. ash	Sol. ash: Insol. ash	Alkalinity insol. ash	Alkalinity sol. ash	Alk. sol. ash: Alk. insol. ash	Conductivity value	Canadian lead number	Winton lead number	Ross lead number	Sy lead value
100	0.70	0.27	0.43	1.59	48	40	0.83	128	2.02	1.34	1.49	0.415
90	0.63	0.24	0.39	1.62	45	38	0.84	117	1.80	1.28	1.37	0.351
80	0.54	0.21	0.33	1.57	44	35	0.80	107	1.38	1.10	1.21	0.308
70	0.47	0.21	0.26	1.24	38	31	0.82	96	1.09	0.98	1.07	0.265
60	0.39	0.18	0.21	1.17	30	28	0.93	85	0.64	0.74	0.86	0.166
50	0.34	0.14	0.20	1.43	26	24	0.92	70	0.37	0.67	0.79	0.126
40	0.31	0.12	0.19	1.58	20	21	1.05	59	0.24	0.56	0.66	0.072
30	0.23	0.09	0.14	1.56	18	17	0.94	47	0.14	0.44	0.52	0.058
20	0.17	0.06	0.11	1.83	14	12	0.86	31	faint turbidity	0.38	0.31	0.032
10	0.06	0.02	0.04	2.00	6	6	1.00	18	no turbidity	0.18	0.23	faint turbidity

TABLE IV—MAPLE SYRUP A. ESTIMATED MAPLE SYRUP CONTENT CALCULATED FROM DETERMINATIONS GIVEN IN TABLE I

Actual per cent maple syrup	Estimated from total ash	Estimated from insol. ash	Estimated from sol. ash	Estimated from alk. insol. ash	Estimated from alk. sol. ash	Estimated from conductivity	Estimated from Canadian lead no.	Estimated from modified Winton lead no.	Estimated from modified Ross lead no.	Estimated from Sy lead value
90	94.7	84.4	101.4	96.4	110.6	92.6	75.7	98.6	94.9	90.3
80	75.4	77.8	73.9	82.1	89.4	84.6	69.9	84.2	89.9	79.8
70	59.6	57.8	60.9	67.9	76.6	74.3	61.1	80.8	84.3	67.0
60	62.3	55.5	66.6	64.3	66.0	66.2	48.7	71.2	78.1	56.7
50	59.6	44.4	69.6	55.4	55.3	57.4	31.0	49.3	74.8	52.3
40	28.1	31.1	26.1	35.7	42.6	47.8	15.9	37.7	69.7	30.4
30	17.5	31.1	8.7	39.3	25.5	36.8	6.2	20.5	58.4	22.0
20	13.2	13.3	13.0	28.6	29.8	25.7	11.0	44.9	15.2
10	7.9	4.4	10.1	17.9	8.5	14.7	0.0	24.7	5.8

TABLE V—MAPLE SYRUP B. ESTIMATED MAPLE SYRUP CONTENT CALCULATED FROM DETERMINATIONS GIVEN IN TABLE II

Actual per cent maple syrup	Estimated from total ash	Estimated from insol. ash	Estimated from sol. ash	Estimated from alk. insol. ash	Estimated from alk. sol. ash	Estimated from conductivity	Estimated from Canadian lead no.	Estimated from Winton lead no.	Estimated from Ross lead no.	Estimated from Sy lead value
90	87.6	92.5	82.7	95.4	92.3	86.5	83.9	91.8	95.3	82.2
80	77.2	62.5	88.5	87.7	78.8	84.7	66.7	81.5	86.0	64.3
70	67.4	65.0	69.2	80.0	73.1	74.1	56.9	70.5	77.9	56.3
60	59.8	55.0	63.5	70.8	59.6	64.1	50.3	61.0	67.4	52.0
50	53.3	50.0	55.8	58.5	53.9	55.9	33.3	50.0	62.8	38.5
40	41.3	30.0	50.0	40.0	50.0	45.3	23.3	37.0	47.7	27.8
30	34.8	22.5	44.2	29.2	44.2	34.1	9.7	26.0	38.4	16.1
20	23.9	15.0	30.8	18.5	26.9	27.6	15.8	21.5	10.9
10	8.7	5.0	11.5	15.4	17.3	14.1	7.5	5.8	4.8

TABLE VI—MAPLE SYRUP C. ESTIMATED MAPLE SYRUP CONTENT FROM DETERMINATIONS GIVEN IN TABLE III

Actual per cent maple syrup	Estimated from total ash	Estimated from insol. ash	Estimated from sol. ash	Estimated from alk. insol. ash	Estimated from alk. sol. ash	Estimated from conductivity	Estimated from			
							Canadian lead no.	Estimated from Winton lead no.	Estimated from Ross lead no.	Estimated from Sy lead value
90	90.0	88.9	90.7	93.7	95.0	91.4	89.1	95.5	91.9	84.6
80	77.1	77.8	76.7	91.7	87.5	83.6	68.3	82.1	81.2	74.2
70	67.1	77.8	60.5	79.2	77.5	75.0	54.0	73.1	71.8	63.9
60	55.7	66.7	48.8	62.5	70.0	66.4	31.7	55.2	57.7	40.0
50	48.6	51.9	46.5	54.2	60.0	54.7	18.3	50.0	53.0	30.4
40	44.3	44.4	44.2	41.7	52.5	46.1	11.9	41.8	44.3	17.3
30	32.9	33.3	32.6	37.5	42.5	36.7	6.9	32.8	34.9	14.0
20	24.3	22.2	25.6	29.2	30.0	24.2	...	28.4	20.8	7.7
10	8.6	7.4	9.3	12.5	15.0	14.1	...	13.4	15.4	...

greater influence of experimental errors in the ash determinations in mixtures of low, as compared with those of high, maple content. In the 10 per cent mixtures the actual quantity of insoluble ash weighed was in each instance one milligram, while the quantities of tenth normal acid used were 0.20, 0.45 and 0.30 cc., respectively, in the soluble ash of Syrups A, B, and C, and 0.50, 0.50 and 0.30 cc. in the insoluble ash. A similar variability is noticeable in most of the other values for the mixtures of low maple content.

The true Winton and Ross lead numbers (Syrups B and C) and the conductivity value come nearest to decreasing proportionally to the maple content. The conductivity value gives estimated results a little higher than the actual, with the single exception of the 90 per cent mixture in case of Syrup B. That this exception is not due to experimental error is evidenced not only by the fact that repetition of the measurement on this syrup confirmed the result at first obtained, but that in the case of four other syrups, 90 per cent mixtures gave estimated values of 86.6, 87.0, 87.2, and 87.3. In this respect, accordingly, Syrups A and C appear exceptional rather than Syrup B. Accordingly, small adulteration with cane sugar appears often to have somewhat more than its proportional effect on conductivity, while greater adulteration has always less than its proportional effect.

suggested that our high results might be due to our neglect to observe his caution to use only freshly boiled distilled water in diluting the syrup. Unfortunately we were not able to test this point with Syrup B as our material was exhausted. We have, however, made a series of experiments on some of the mixtures of Syrup C, the results of which are given in Table VII. No

TABLE VII—COMPARISON OF ROSS LEAD NUMBERS ON MIXTURES OF SYRUP C, USING FRESHLY BOILED AND UNBOILED WATER

Actual per cent maple syrup	Ross lead number with freshly boiled water	Calculated per cent maple syrup	Ross lead number with unboiled distilled water	Calculated per cent maple syrup
100	1.42		1.49	
80	1.17	82.0	1.21	81.2
50	0.78	54.9	0.79	53.0
20	0.32	22.5	0.31	20.8

difference of consequence was observed due to the boiling of the water. In order to make a further study of the Winton and Ross methods we prepared two composite samples (D and E) from 100 pure syrups made in the season of 1913. The syrups from which these composites were made were obtained directly from the sugar bushes of Quebec and Ontario by graduate representatives of the College, so that there can be no doubt as to their purity. Mixtures of these syrups with cane syrup were made up and the Ross and Winton lead determinations made upon each,

TABLE VIII—COMPARISON OF WINTON AND ROSS LEAD NUMBERS ON SYRUPS D AND E

Syrup D				Syrup E			
Actual per cent maple syrup	Winton lead no.	Maple content estimated from Winton lead no.	Ross lead no.	Actual per cent maple syrup	Winton lead no.	Maple content estimated from Winton lead no.	Ross lead no.
100	1.71	...	2.01	100	1.635	...	2.155
90	1.56	91.2	1.85	90	1.325	81.0	1.94
80	1.30	75.7	1.63	80	1.18	72.2	1.75
70	1.14	66.7	1.41	70	1.06	64.8	1.625
60	1.03	60.2	1.40	60	0.825	50.5	1.355
50	0.875	51.2	1.19	50	0.645	39.4	1.12
40	0.605	35.4	0.825	40	0.46	28.1	0.905
30	0.425	24.9	0.76	30	0.29	17.7	0.72
20	0.265	15.5	0.43	20	0.145	8.9	0.445
10	0.09	5.3	0.135	10	0.060	3.7	0.190

The Ross lead number when determined by the original method (Syrups B and C) does not decrease as rapidly as the actual maple syrup content. (In the case of Syrup A where the determinations are made on a quantity of syrup equivalent to 25 grams of dry sugar the results obtained are high throughout and further from the actual proportions of maple syrup than are those obtained without the use of potassium sulfate.) These results—particularly those on Syrup B (Tables II and V)—are not in agreement with Dr. Ross's experience, and in correspondence with us he

freshly boiled water being used in the Ross method. As will be seen from the results which are tabulated in Table VIII, the Ross method gives estimated results much closer to the actual maple content than does the Winton method. Especially is this the case in regard to Syrup E. In most instances the estimated results with the Winton method are lower than the actual maple content, while on the other hand the Ross method gives results slightly higher than the actual.

The Canadian lead number drops off much more rapidly than the actual maple syrup percentage and

vanishes in the three series at a maple content of 20 per cent. This fact gives the Canadian method a distinct advantage as far as the detection of small adulteration is concerned, but renders it useless for distinguishing compound maple syrups containing none. Moreover, the advantage of the Canadian method for the former purpose is somewhat offset by the great variability of the Canadian lead number in genuine maple syrups. In its investigation of some 450 Canadian syrups of the season of 1911, obtained directly from the makers accompanied by a declaration of genuineness,¹ the Laboratory of the Inland Revenue Department found twelve syrups with values below that adopted in the standard, *viz.*, 1.70. Six samples yielded lead values of over 4.50, and of these three were above 5.00. In an uncompleted investigation of 125 genuine Canadian syrups of the season of 1913 we have found even a greater variation in the Canadian lead number, 9 samples having values above 4.50, 8 of which are also above 5.00. As will be seen by referring to the Canadian lead numbers in Table II, a syrup of high lead value may be adulterated with a comparatively large proportion of cane sugar without falling below the Canadian standard. Syrups A and C, however, with original lead values of 2.26 and 2.02, respectively, have already reached the limit of the standard when the adulteration amounts to 10 per cent.

The Sy lead number, like the Canadian, drops off more rapidly than the maple content. But it does not show this propensity to the same degree as the Canadian value. We are unable to see any advantage in Sy's method over the other methods which would compensate for the extra time and labor involved in making the determination.

RANGE OF VARIATION IN GENUINE SYRUPS

The delicacy of any method of detecting adulteration of maple syrup with pure sucrose obviously depends upon: (1) The limits of natural variation of the value in question in genuine syrups. (2) The rate at which the value falls off as the proportion of genuine syrup is decreased. As we have seen, the Canadian lead value excels in the second point but not in the first. The range of variation of the different values may readily be seen from Table IX, which

TABLE IX—RANGE OF VARIOUS ANALYTICAL VALUES IN GENUINE MAPLE SYRUPS. EXPRESSED IN PERCENTAGE OF THE MINIMUM

Investigator	Total ash	Winton lead no.	Malic acid value	Canadian lead no.	Conductivity value
Bryan.....	147	151(a)	452
McGill.....	100	127(b)	287	380	...
Snell and Scott.....	125	190	329	331	109

(a) Original Winton method. (b) Modified.

shows percentage variation of the different values in the natural product as found by Bryan, McGill, and ourselves. Bryan's figures were obtained from 481 samples of maple syrup representing all the maple-producing states of the Union and the Province of Quebec. McGill's figures on the Canadian lead number are based upon analyses of 456 samples of Cana-

dian syrups; those on Winton lead number, total ash and malic acid upon a study of 47,115 and 452 of these samples, respectively. Our limits for the conductivity method are the result of measurements made upon over 200 syrups. It will be noticed that the range is somewhat wider than that reported in the first paper of this series, *viz.* 82%. This is due to the fact that since the publication of the paper on electrical conductivity we have found syrups which gave conductivity values above the maximum previously obtained (200) and which from our present information we must regard as genuine. We have, however, found none below the minimum reported (110). Our figures for the other values are based upon an uncompleted investigation of 125 samples of Canadian syrup of the season of 1913 and are to be regarded as merely tentative. When the investigation is completed the range of some of the values may prove to be narrower than here reported. From the figures given in Table IX it is evident that the conductivity value shows the narrowest limits of variation of any of the data.

COMPARATIVE PRECISION OF LEAD METHODS

The Laboratory of the Canadian Inland Revenue, which originated the Canadian lead method, admits that the Winton method gives more precise results, *i. e.*, closer duplicates, than can be obtained with the Canadian method. Our own experience is to the same effect. It occurred to the authors that it might be possible to combine the advantages of these two methods by using the same proportion of lead subacetate solution as in the Canadian method, and determining the amount of residual lead in solution as in the Winton method. Some experiments have been carried on in this connection, the results of which will be published in a subsequent paper.

MODES OF WASHING PRECIPITATE IN CANADIAN LEAD METHOD

Experiments have also been made upon the effect of temperature and volume of wash-water upon the weight of the lead subacetate precipitate as obtained by the Canadian method. The results given in Table X clearly indicate that wash waters of 80° and 100° C.

TABLE X—EFFECT OF VARIATIONS OF TEMPERATURE AND VOLUME OF WASH WATER UPON THE CANADIAN LEAD NUMBER

		Syrup I			
		Total quantity of wash water (a)			Average
Temp. of wash water 80° C.		50 cc.	100 cc.	150 cc.	
1st time.....	4.56	4.29	4.20	
	4.52	4.32	4.62	
	4.68	4.63	4.12	
2nd time.....	4.80	4.60	4.21	
	
	
Average at 80°.....		4.64	4.46	4.29	4.46
100° C.					
1st time.....	4.77	4.37	4.70	
	4.66	4.50	
	4.84	4.26	4.36	
2nd time.....	4.35	4.42	
	
	
Average at 100°.....		4.76	4.33	4.50	4.53
Average.....		4.70	4.40	4.40	
Max. deviation.....		0.18	0.23	0.30	

(a) Applied in five equal portions in every instance.

¹ Lab. of the Inland Revenue Dept., Ottawa, *Bull.* 228 (1911).

Syrup II

Total quantity of wash-water(a)

Temp. of wash water 80° C.	50 cc.	100 cc.	150 cc.	Average
1st time.....	2.83	2.40	2.58	
	2.92	2.54	2.69	
2nd time.....	2.95	2.74	2.75	
	2.98	2.75	2.79	
Average at 80°	2.92	2.61	2.70	2.74
100° C.				
1st time.....	2.93	2.72	2.51	
	2.82	2.70	2.65	
2nd time.....	2.82	2.81	2.43	
	2.98	2.76	2.54	
Average at 100°.....	2.89	2.75	2.53	2.72
Average.....	2.91	2.68	2.62	
Max. deviation.....	0.09	0.28	0.19	

(a) Applied in five equal portions in every instance.

give identical results. Higher results are obtained with 50 cc. of wash water (applied in five portions) than with 100 cc. or 150 cc. There is no material difference between the results obtained with 100 cc. and with 150 cc. of wash water.

MODES OF REDUCTION OF LEAD NUMBERS TO DRY MATTER BASIS

In the investigation made by the Laboratory of the Inland Revenue Department preliminary to the setting of standards, the Canadian and Winton lead determinations were made upon fixed quantities of syrup (5 grams and 25 grams, respectively) and the results calculated to a dry matter basis. The standards, however, prescribe the use of a quantity of syrup equivalent to the same fixed quantity of *dry matter*, *i. e.*, 5 grams and 25 grams of dry matter, respectively. We have made a comparison of results obtained directly by the methods of the Canadian standard with those obtained by calculation from the determinations on the wet basis. As will be seen from Table XI,

TABLE XI—COMPARISON OF LEAD NUMBERS ON DRY BASIS, ACTUAL AND CALCULATED

Syrup number	Canadian lead method			Winton lead method		
	Actual lead no.	Calculated lead no.	Difference	Actual lead no.	Calculated lead no.	Difference
1	1.80	1.36	0.44	1.35	1.53	0.18
2	3.20	2.95	0.25	1.96	2.11	0.15
3	3.02	2.63	0.39	1.98	2.20	0.22
4	2.86	2.51	0.35	2.01	2.16	0.15
	Average, 0.36			0.18		

with the Canadian method the results obtained by calculation to a dry basis are lower than those determined directly upon the dry basis, the average difference on the four syrups being 0.36. With the Winton method, on the other hand, the calculated results are uniformly higher than those directly determined, the average difference in this case being 0.18. All results given are the average of closely agreeing duplicates. It would appear, therefore, that material differences exist between the results obtained, on the one hand, by determination upon a fixed quantity of syrup and calculation to a dry basis and, on the other hand, by direct determination upon a definite quantity of dry matter.

THE BLANK IN THE WINTON METHOD

In making the determination of lead in the blank for the Winton method, Bryan recommends the addition of acetic acid to the lead subacetate solution to prevent formation of a precipitate upon the addition of water, "as pure sugar would do."¹ Upon making determinations in duplicate on two blanks, one treated with acetic acid, the other with 25 grams cane sugar syrup, we found that smaller amounts of lead were held in solution by the cane sugar than by the acetic acid. This was the case, whether the determinations were made immediately upon the unfiltered blank or upon the settled (3 hours) and filtered blank, as will be seen from the figures of Table XII. It would

TABLE XII—EXPERIMENT ON WINTON BLANK

	Weight of lead sulfate precipitate	
	Immediately unfiltered	At end of 3 hours filtered
Acetic acid used as clarifier in blank.....	0.1593	0.1600
25 grams cane sugar syrup in blank.....	0.1571	0.1558

seem to be more rational to make the Winton blank in the presence of cane sugar syrup rather than with acetic acid, as in this way we should approximate more closely to the conditions obtaining in the determinations upon maple syrup.

SUMMARY

1. The rates at which the conductivity value, ash data and various lead values fall off as maple syrup is diluted with cane sugar syrup are determined for three samples of maple syrup.
2. The range of variation of these data in genuine syrups is studied with reference to the work of Bryan and McGill, as well as to our own work.
3. The Canadian lead value shows the most rapid falling off.
4. The conductivity value shows the narrowest range.
5. The Winton lead method gives better agreement of duplicates than the Canadian method.
6. In the Canadian method no material difference is obtained by washing the precipitate with water at 80° and 100° C. Practically identical results are obtained with 100 cc. and 150 cc. wash water, but higher results with 50 cc.
7. Results obtained in the Canadian method, using the quantity of syrup containing 5 grams of dry matter, are higher than those obtained with use of 5 grams of syrup and calculated to the dry basis. On the other hand, in the modified Winton method, prescribed in the Canadian standards, lower results are obtained with the use of the quantity of syrup containing 25 grams dry matter than when 25 grams syrup are used and the results calculated to the dry basis.
8. The use of cane-sugar syrup instead of acetic acid in the Winton blank is suggested.

(The expenses of this investigation were defrayed out of the grant of the Dominion Government for the advancement of agriculture, 1912.)

MACDONALD COLLEGE
QUEBEC, CANADA

¹Bryan, *loc. cit.*, p. 18.

ON THE PREPARATION OF NEUTRAL AMMONIUM CITRATE SOLUTION¹

By PAUL RUBINICK AND W. L. LATSHAW

It has been the custom in this laboratory for several years past to determine the strength of neutral ammonium citrate solution by the analytical method recommended by the Committee on Ammonium Citrate Solution of this Division in 1909,² except that no attempt was made to determine the citric acid content by titrating back the residue after distillation of the ammonia. It was found simpler and easier to determine the strength in this way and to calculate from this strength the extent of dilution necessary to bring the solution to the strength recommended, *i. e.*, 43.7 grams of ammonia per liter, than to dilute to the required specific gravity by cut-and-try methods. A determination of the specific gravity of the solution thus prepared is always made as a final check and is always found to be 0.09 ± 0.001 , substantially as required by the official method.³

The determination of the neutrality proper, however, has not been made by determining the citric acid as recommended by the committee, but is made by the indicator method recommended by Hand,⁴ which has proven fairly satisfactory in our hands so far as ease of manipulation and simplicity were concerned.

The electrical conductivity methods proposed by Hall and Bell⁵ and later by Patten and Robinson⁶ as well as the extraction and temperature methods proposed by Bell and Cowell⁷ do not seem applicable to the problem as presented in routine fertilizer work for various reasons, chiefly because of the difficulties of manipulation involved. A most practical method of attacking the problem was advised by Patten and Marti⁸ and presented at the last meeting of this Division in Milwaukee. The great advantage of this method lies both in its simplicity and ease of accurate reproduction, as well as in the fact that it is based upon reliable and accurate physico-chemical measurements summarized in a definite strength of both ammonia and citric acid.

It became a matter of interest to compare this method with the method used in this laboratory heretofore as described above, and the following is an account of the preliminary work undertaken and of the results so obtained.

Two solutions of ammonium citrate were prepared as follows:

Solution I upon analysis by the Patten and Marti method showed a content of 158.1 grams of citric acid and 37.23 grams of ammonia per liter. From this the proper correction for both citric acid and ammonia were calculated and a re-analysis of the corrected solution showed a content of 168.6 grams of citric acid

and 44.54 grams of ammonia per liter. The gravity of this solution was 1.09. This solution was assumed to be practically neutral and of the proper strength, although when tested by the indicator method of Hand it seemed to be very slightly acid. This was in accordance with the ratio of ammonia to citric acid, namely 1 : 3.786 instead of 1 : 3.765.

Solution II was made up of a higher concentration than that required by the official method and was then brought to neutrality as follows:

Instead of following strictly the method of Hand a series of tubes was prepared from Solution I as described by Hand, namely adding 5 cc. of the ammonium citrate solution to 45 cc. of neutral water containing the prescribed amount of azolitmin indicator. One of these tubes was left unchanged and to the remainder were made successive additions, differing by 0.5 cc. each, of *N*/10 ammonia and *N*/10 citric acid, respectively. From these tubes the one apparently nearest neutral was chosen and Solution II was then adjusted to this color by the method of Hand. Instead of comparing the tubes as described by him, however, we found it much easier to compare them in a Craven-Jennings colorimeter¹ in the same manner as in nesslerization of water.

Solution II was then analyzed by the Patten and Marti method and was found to contain 179.2 grams of citric acid and 47.80 grams of ammonia per liter, giving a ratio of 1 : 3.748 as against 1 : 3.765, the ratio given by Patten and Marti. Solution II was then brought to a gravity of 1.09.

We now had two solutions, one of which (Solution II) was obviously slightly alkaline, the other (Solution I) slightly acid. Comparative analyses of a sample of acid phosphate were made with these two solutions, giving the following results:

PERCENTAGES INSOLUBLE P_2O_5 BY	
Solution I	Solution II
1.10	1.11
1.11	1.10
Lost	1.12

These results would indicate that the variation of these solutions from the ratio given by Patten and Marti was not sufficient to affect the results obtained on the sample of acid phosphate in question. Further work on this subject is in progress.

CHEMICAL LABORATORY OF ARMOUR & COMPANY
UNION STOCK YARDS, CHICAGO

A STUDY OF THE PEMBERTON-KILGORE METHOD FOR DETERMINATION OF PHOSPHORIC ACID

By P. L. HIBBARD

Received Aug. 4, 1913

After using the Pemberton-Kilgore volumetric method for phosphoric acid quite successfully for some time, sources of error in it became apparent. Endeavor to avoid these errors led to the making of this study, which is now published with the hope that others may be helped in the use of this very good method.

In the beginning it is well to understand that the method is not, nor can it be made scientifically exact. Good results obtained in the use of it must always be

¹ Supplied by the Bausch & Lomb Optical Company.

¹ Paper presented at the 48th meeting of the A. C. S., Rochester, September 8-12, 1913.

² W. D. Richardson, *et al.*, *THIS JOURNAL*, **1**, 616 (1909).

³ *Bur. Chem., Bull.*, **107**, page 1.

⁴ *Ibid.*, **132**, page 11.

⁵ *J. Am. Chem. Soc.*, **33**, 711 (1911).

⁶ *THIS JOURNAL*, **4**, 443 (1912).

⁷ *J. Am. Chem. Soc.*, **35**, 49 (1913).

⁸ *THIS JOURNAL*, **5**, 567 (1913).

due to a proper balancing of tendencies to error. Nevertheless, with proper handling, it is capable of giving results which for accuracy and reliability compare favorably with those obtained by most analytical methods in common use, and which are obtained with an ease and speed not equalled by any other method for determination of phosphoric acid known to the writer. Much similar work has been done by others. (See Bibliography.)

Publication of this study has been long delayed, with the hope of better clearing up several points. Pressure of other work now makes it likely that this is very remote. But for practical purposes the work is complete and is now given publicity with the hope that it may assist some to successfully use the Pemberton-Kilgore method, who would not otherwise overcome some of its difficulties.

This work includes a study of the influence of the chief factors likely to have any bearing on the successful use of the method, as apparent to the writer. The method is not well adapted for estimating very small amounts of phosphoric acid. Many of the results are given in tabular form for easy reference. This is followed by a summary and bibliography.

A. PRINCIPLES OF THE METHOD

The phosphate solution is mixed with an acid solution of molybdic acid, which causes precipitation of an acid double salt of phosphoric and molybdic acids of uniform and definite composition (E 26). This salt, here spoken of as yellow precipitate, is filtered out, washed free of other acid, and its acidity determined by titration with standard caustic alkali, which thus measures the amount of P_2O_5 in the solution analyzed. Apparently this should give scientifically exact results. In practice this is not true because of the influence of the numerous other substances usually present in the phosphate solution. Inexperienced operators will usually get as good results with this method as with most others. Experienced analysts will need considerable practice with it before then can safely rely on their results, though it is hoped that careful reading of this study will soon enable such persons to use it very successfully. In case but few determinations are to be made at one time, it is scarcely worth while to prepare the apparatus and solutions needed. The gravimetric method would be more convenient.

The method is suitable for determination of P_2O_5 in almost any substance, with great speed and adequate accuracy. After the solution of the phosphate is prepared the assay may be completed in 20 minutes or in much less time, at slight sacrifice of accuracy. In the analysis of fertilizers by this method, I have been able to complete 21 determinations, including weighing out to final result, in a little over six hours of actual working time, on various occasions. About one-third of those were determinations of citrate-insoluble P_2O_5 which require much more time to prepare the solutions. After the solutions were prepared I have been able to precipitate, wash and titrate to final result 22 samples in two and one-third hours.

B. THE FILTER AND PREPARATION OF ASBESTOS

Lack of a suitable filter is the probable cause of more failures in the use of this method than any other one thing. The usual paper filter, or the Gooch crucible, is not well suited to the work, and any one depending on them is likely soon to be discouraged. The filter tube described by Kilgore is very satisfactory (G 7). Commonly known as a carbon tube or sugar filter, this is a glass tube about $1\frac{1}{4}$ inches wide, $2\frac{1}{2}$ inches long, open at one end and narrowed at the other end to a stem $\frac{1}{4}$ inch diameter and 2 inches long. A perforated porcelain disk $1\frac{1}{8}$ inches diameter has a stiff piece of platinum or copper wire 5 inches long fastened in its center. By extending into the narrow stem this wire holds the disk level in the bottom of the filter tube. The disk supports a layer of prepared asbestos about $\frac{1}{8}$ inch thick which forms the filter. The stem of the filter tube is pushed through one hole of a two-hole rubber stopper which is placed in the mouth of an ordinary 12-ounce wide mouth bottle. A bent glass tube in the other hole of the stopper is connected with the vacuum pipe. Suction equal to 10 inches of mercury is sufficient. In forming the filter, suction should not be applied until most of the water has run out of the asbestos pulp after it is poured into the filter tube.

A suitable quality of asbestos is very important for rapid and clear filtering. In order to prepare the asbestos, shred it to small pieces, pack into a wide mouthed flask, cover with dilute HCl (1 to 3). Place the flask in a water bath and heat to boiling several (five) hours. (Cannot well be heated over flame.) Filter on a Buchner filter, wash free of acid, return to the flask and cover with 5 per cent caustic soda, heat again in a water bath three hours, filter, wash free of alkali, then with dilute acid, and finally with water till free of acid. The fine part must now be removed by decantation. (Attempts to remove the fine asbestos by an elutriation process were not very successful.) The asbestos is suspended in a large volume of water, in a tall jar or cylinder, allowed to stand about five minutes, till the valuable coarser part is settled. The milky liquor in the upper $\frac{2}{3}$ of the jar is now siphoned off, the jar again filled with water and the asbestos stirred through it; after a few minutes the milky liquor is again drawn off. The fine asbestos in the liquor drawn off is of no value for filtering and if left with the coarse part, clogs the filter, making it very slow in operation. The decantation must be repeated five or six times till the liquor drawn off contains very little suspended matter. The remaining medium coarse asbestos is now ready for use. To make a quick-acting filter the fibers should be long and rather stiff so that the filtering bed will be somewhat springy and remain very porous under pressure. If the asbestos fiber is very soft and thread-like, the filter bed becomes compact and filters very slowly. After using in a determination, the asbestos may be recovered for using again, by washing with alkali, then acid and again decanting to remove fine material. The filtering tubes prepared with this asbestos are used much as the gooch crucible would be. With this apparatus and

properly prepared asbestos, the operation of filtering and washing an ordinary P_2O_5 precipitation need not consume more than five minutes.

If an ordinary paper filter be used, there is danger of decomposition of the precipitate by the long washing necessary to remove all acid from the filter paper. This decomposition may be prevented by the presence of 2 per cent of potassium nitrate in the wash water. If paper is used, there is danger of reduction of the molybdate during the titration, after the solution becomes alkaline, thus producing a bluish color, which obscures the end point in the final titration back with acid. The ammonium phosphomolybdate precipitate packs very much during filtration by suction so that if there is much of the precipitate, it makes so deep a layer in the ordinary size of gooch crucible, that filtration and washing are slow. Besides, the gooch is not a convenient dish from which to transfer the precipitate and asbestos back to the precipitating flask. Both of these defects are avoided by use of the carbon filter tube of the size mentioned; besides, the tube has much greater capacity to hold liquid than the gooch, which is a great advantage when several are operated simultaneously.

The water used for washing the yellow precipitate must be neutral and free of organic matter, ammonia or CO_2 compounds.

C. EXPLANATION OF METHODS AND SOLUTIONS USED

Details of the method of operating are given under Section D.

For nearly all of the work here reported a solution of sodium phosphate was used, usually containing about three grams per liter. This makes about 20 mg. P_2O_5 in 25 cc., the amount usually taken for each test. For measuring the separate portions, a 25 cc. automatic overflow pipette was used. Its delivery was very constant and reliable. During the course of the work several different phosphate solutions were made and used. For this reason the actual P_2O_5 taken for each set of experiments was somewhat variable, and the correct amount is usually given at the beginning of each table. With some exceptions figures given are the result of two or more closely agreeing determinations; in many cases, numerous determinations were made. In some of the less important matters only the figures given were obtained.

The molybdate solution used was made up according to the method of the A. O. A. C., *Bulletin* 107, p. 4, Bureau of Chemistry, United States Department of Agriculture. One liter contained about 50 grams MoO_3 (85 per cent), 72 cc. ammonia (sp. gr. 0.90) and 250 cc. HNO_3 (sp. gr. 1.42). This was freshly filtered at time of using, and to each 100 cc., 5 cc. HNO_3 (sp. gr. 1.42) were added. In most cases 25 cc. of NH_4NO_3 (60 per cent solution) = 15 grams were used in each test.

In experimenting with the various substances, a concentrated solution of each was made and various amounts of it were added to the phosphate solution before making the volume up to 100 cc. with water. For convenience complete working details of the method are here given.

D. WORKING DETAILS OF THE VOLUMETRIC METHOD

For this process the solution may be prepared by any of the methods given in E 24, except by the use of sulfuric acid. For the precipitation, a wide mouthed Erlenmeyer flask of about 400 cc. capacity is convenient. Transfer to the flask, by means of a pipette, an aliquot of the phosphate solution such that it will contain 10 to 30 mg. phosphoric acid. It is desirable to have as nearly 20 mg. as convenient. Neutralize the aliquot taken by adding a slight excess of ammonia, then nitric acid to faint acidity; then add 25 cc. of ammonium nitrate, 60 per cent solution; then water to bring the total volume to about 100 cc. In case very small amounts of phosphoric acid are present, it is better not to increase the volume more than necessary, leaving it less than 100 cc. if convenient. Place the flask in the water bath at $65^\circ C.$ and after a few minutes, when warm, add excess of ammonium molybdate solution, mix, and let stand at 65° for 15 minutes. (Temperature in the flask is usually 2 or 3 degrees lower than in the bath.) The amount of molybdate solution is varied in proportion to the phosphoric acid present.

The minimum amount to be used is 20 cc. and if a proper aliquot of the phosphate solution is taken, 40 cc. will be sufficient for almost any sample. The molybdate solution must be filtered immediately before using; then add to it 5 cc. of nitric acid for each 100 cc. of molybdate solution. In case there is very little phosphoric acid present, or, if the solution contains much silica, it is better to keep temperature at 50 to 55 instead of 65. It should never be higher than 65 on account of danger of precipitating molybdic acid, and the time should not be much over 15 minutes at this temperature. After expiration of the time, filter on asbestos in filter tube above described supported on a 12-ounce wide mouth bottle. Wash with pure water which must be neutral. By using 20 to 30 cc. of water for each washing, the precipitate is usually free of acid by the time the bottle is full. In order to test for freedom from acid, transfer the filter to a clean bottle in which collect some of the washings (20 to 30 cc.), add a few drops of phenolphthalein, then one drop of standard alkali. If the red color is persistent, the washing has been sufficient. Rinse off the outside of the filter tube with water. Invert it into the mouth of the flask and by means of the wire in the disk, push the precipitate out into the flask. Rinse out clean with water, into the flask. Now titrate with the standard alkali, $NaOH$ or KOH with continual shaking, until the yellow precipitate has completely disappeared. This disappears gradually. Take care not to use a large excess of alkali. Two or three cc. excess is best. After complete disappearance of the yellow precipitate add $\frac{1}{2}$ cc. phenolphthalein solution and titrate back to colorless with standard nitric acid, which is usually of the same strength as alkali. The standard alkali used is of such strength that 1 cc. is equivalent to 1 mg. of P_2O_5 (32.38 normal). From this may be calculated the amount of phosphoric acid present.

E. DETAILED STUDY OF THE CHIEF CONDITIONS AND SUBSTANCES CONCERNED IN THE USE OF THE VOLUMETRIC METHOD

In general, except when otherwise stated, each test was conducted about as described under D.

1. Temperature

The yellow precipitate separates from the usual molybdate solution more or less rapidly, according to temperature. Hence, it is important to measure this effect at various temperatures.

TABLE I

A. 20.3 mg. P_2O_5 present			B. 21.3 mg. P_2O_5 present		
Time heated	Mg. P_2O_5 found		Time heated	Mg. P_2O_5 found	
	°C.			°C.	
15	40	18.9(a)	15	50	20.6
15	50	20.2	30	50	20.8
15	60	20.1	60	50	21.0
15	65	20.3	120	50	21.3
15	70	20.8	60	65	21.6
...	15	65	21.3

(a) Very imperfect precipitation.

The precipitate formed at temperatures below 40° is very finely divided and difficult to filter properly, though it becomes fairly good if allowed to stand over night. Yet the result is low. A shows effects of variations in temperature for a fixed time. B shows effect of varied time at fixed temperature. High temperature promotes complete and rapid separation of yellow precipitate also of MoO_3 . At low temperature MoO_3 does not separate so soon, but the yellow precipitate is also slow in forming, and too finely divided to filter well, so a medium point is selected at which the main evils are avoided and a reliable result obtained. For this work the official conditions seem as good as any, 15 minutes at 65° with 100 cc. volume, though it is quite possible that a different set of conditions would do as well if properly worked out. Thus, a higher temperature with shorter time would do very well, except that there is greater danger of separation of MoO_3 if temperature is not quickly lowered. Lower temperature with longer time is very frequently used, and is safer, the only objection being longer time necessary.

2. Time

Table I indicates that time has a very important effect on separation of MoO_3 . This is better shown in Table II in which time is varied but temperature constant.

TABLE II
20.3 mg. P_2O_5 present

Time heated	Temperature °C	P_2O_5 found
1 min.	65	19.9
5 min.	65	20.1
15 min.	65	20.3
30 min.	65	20.4
60 min.	65	20.8
15 min.	65 then stood	...
24 hrs.	20	20.3

The last result shows that after the precipitation is properly completed at the elevated temperature, the result is not changed by allowing it to stand 24 hours at room temperature.

3. Volume or Concentration

The volume in which precipitation takes place has a very important effect on the character of the precipitate. In a concentrated solution of P_2O_5 , the precipitate is too finely divided and does not filter and wash well. In a dilute solution the precipitate is slow in forming and is likely to be deficient in quantity. Table III indicates these effects.

TABLE III

A. 20.3 mg. P_2O_5 present		B. 4.07 mg. P_2O_5 present	
Volume Cc.	Mg. P_2O_5 found	Volume Cc.	Mg. P_2O_5 found
50	20.2	25	4.05
100	20.3	50	4.00
150	20.3	100	3.50
300	19.5

In this table all quantities were constant except volume. But if molybdenum is increased in proportion to total volume, the P_2O_5 found is nearly correct as is indicated in Table IV.

4. Proportion of Molybdenum

Whatever may be the composition of the yellow precipitate it is fully established by experience that much more molybdenum must be present in the solution than is necessary to combine with the P_2O_5 present. Twice as much is commonly used, often much more. This excess tends to separate from the solution at elevated temperatures and contaminate the yellow precipitate. Herein is perhaps the greatest inherent source of error in the volumetric method. Ammonium nitrate in the solution reduces the amount of molybdenum necessary for complete precipitation of P_2O_5 , also, promotes separation of MoO_3 . HNO_3 has the opposite effect. Hence, all these must be considered in adjusting the solution which is discussed under heading 9.

Table IV indicates effects of varying molybdenum, all other quantities remaining constant, except as indicated. In B the proportion of molybdenum to phosphoric acid is relatively high, and high results are shown. In C the opposite is true.

TABLE IV

A. 20.3 mg. P_2O_5 present			B. 4.07 mg. P_2O_5 present			C. 40.7 mg. P_2O_5		
Molybdate reagent used. Cc.	Total volume. Cc.	Mg. P_2O_5 found	Molybdate reagent used. Vol.	Total volume. Cc.	Mg. P_2O_5 found	Molybdate reagent used. Vol.	Total volume. Cc.	Mg. P_2O_5 found.
15	100	19.6	5	100	3.90	30	100	39.6
20	100	20.1	10	100	4.35	40	100	39.9
25	100	20.2	15	100	4.40	50	100	40.0
30	100	20.3	20	100	4.40	75	125	40.2
40	100	20.3	100	125	40.1
60	100	20.5

5. Nitric Acid

Free acid must be present in order that the yellow precipitate may be formed as shown under *Effect of Free Acids* (E 8). Nitric is the most suitable acid (E 25). Contrary to the effect of NH_4NO_3 it tends to prevent separation of both the yellow precipitate and of MoO_3 , i. e., both are soluble in acid of sufficient concentration. As shown in Table VIII, less than

the usual amount allows MoO_3 to separate, causing high results, while more than twice the usual amount has but little solvent effect on the precipitate.

c. Ammonium Nitrate

Ammonium nitrate, though formed in the reaction, is not necessary except to produce a desirable physical condition of the precipitate and render it less soluble in the liquid. It promotes the separation of MoO_3 , thus causing high results, but if it is absent the precipitate is very finely divided, hence, difficult to filter, and result is low. Large excess of ammonium nitrate causes an amorphous precipitate, which passes through the filter during washing, yet results are high—due to co-precipitated MoO_3 . Ammonium nitrate may be to some extent replaced by other salts which tend to have similar effects in promoting proper formation and separation to the precipitate. Thus in the presence of NaCl or $(\text{NH}_4)_2\text{SO}_4$, less NH_4NO_3 is required.

TABLE V
Substitution of NH_4NO_3

By NaCl			By $(\text{NH}_4)_2\text{SO}_4$		
NH_4NO_3 Cc.	NaCl Cc.	$\text{Mg. P}_2\text{O}_5$ found	NH_4NO_3 Cc.	$(\text{NH}_4)_2\text{SO}_4$ Cc.	MgP_2O_5 found
15	0	20.3	15	0	20.8
15	4	20.5	3	4	21.3
0	8	20.0	3	8	21.1
5	8	20.3
15	8	20.6
0	16	18.6
10	16	20.2

(This is complicated by action of SO_4 which usually tends to high results.) Therefore, if the solution contains much of some other salt, less NH_4NO_3 need be used. If the full usual amount is used in addition to the other salt present, the bad effects of an excess of the latter are apparent, while if less NH_4NO_3 were used the other substance would not interfere so much.

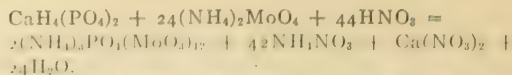
Besides its effects on the precipitate, ammonium nitrate prevents solution of the precipitate by the wash water during filtration, and partially offsets the bad effect of excessive soluble chlorides in some cases.

7. General Effect of Salts in Solution

Below 5 per cent most salts have but slight effect. Iron salts and sulfates are exceptions. Large quantities of all salts examined have similar general effect, though not to the same extent for all. Nitrates are least injurious. Large amounts of soluble salts increase solubility of yellow precipitate and tend to prevent its formation, also, cause it to run through the filter in washing. The only remedy is to decrease the concentration of the salt. Decomposition of the precipitate in washing is largely avoided by presence of 2 per cent of KNO_3 or NH_4NO_3 in the wash water. Molybdic solution or dilute HNO_3 is also effective, but is not permissible in the volumetric method.

8. Effect of Free Acids

The yellow precipitate is soluble in strong acids so that their general effect is to cause low results. But a certain amount of free acid is necessary to form the precipitate according to the equation:



This free acid may be either HCl , HNO_3 , or H_2SO_4 , though HNO_3 is preferable as shown under E 25. Besides being necessary in the reaction, to form ammonium phosphomolybdate, free acid is necessary to prevent separation of MoO_3 and the quantity thus needed is variable depending on the amounts of salts, molybdenum, P_2O_5 and water in a given volume. Free acid is also needed to keep in solution certain bases, as Fe , Cu . The free acid usually present is commonly several times the amount needed in the reaction. According to the equation above, 1 part P_2O_5 requires 16.2 parts MoO_3 and 18.6 parts HNO_3 . If the solution contains 0.02 per cent P_2O_5 this would need for the reaction 0.372 gram HNO_3 . However, 30 cc. of the official molybdate solution used in this case would contain nearly seven grams HNO_3 . The relation of these various substances may well be discussed under the heading:

9. Proportion between P_2O_5 , HNO_3 , NH_4NO_3 , Molybdenum and Volume

Fifteen to thirty mg. P_2O_5 is the most convenient amount. There is no advantage in more P_2O_5 as sensitiveness of end point decreases in proportion as P_2O_5 increases, so that greater accuracy is not obtained by use of larger amounts of P_2O_5 . This is one of the weakest points of the method and makes the result somewhat uncertain for high percentages of P_2O_5 . For small amounts of P_2O_5 , 15 mg. or less, it is better to keep the volume below 100 cc. in order to obtain rapid separation of yellow precipitate. In this case less NH_4NO_3 should be used. The relation between NH_4NO_3 and HNO_3 in the solution may be somewhat a matter of personal choice. It is shown by Hundeshagen (G 34) that at least 26 mol. HNO_3 to 1 PO_4 are necessary, and up to 80 do no harm; above that causes solubility of precipitate. But this was in the presence of but little NH_4NO_3 . In my work, which is essentially according to the method of the Official Agricultural Chemists, 15 per cent NH_4NO_3 is used, in general, and with this about 7 per cent free HNO_3 (supplied by molybdate solution). This is about 3 times as much acid as Hundeshagen recommends. The purpose of NH_4NO_3 is to promote rapid and complete separation of precipitate but it also promotes easy separation of MoO_3 which tendency is counteracted by free HNO_3 . This free acid which is contained in the molybdate solution helps preserve the reagent and tends to prevent separation of MoO_3 from this solution (molybdate) while standing before use, as well as after it is mixed with P_2O_5 solution. If less NH_4NO_3 is used, less HNO_3 should be used, to avoid solubility of precipitate.

In order to secure complete separation of the yellow precipitate in a short time, the amount of molybdenum used should be at least twice the amount necessary to combine with P_2O_5 . NH_4NO_3 helps to reduce the amount of molybdenum thus needed. But the greater the excess of molybdenum present the greater is the danger of separation of free MoO_3 ; hence, the limit to 2 or 3 times the amount entering the precipitate.

In case of very small amounts of P_2O_5 results are usually high if large excess of molybdenum is used. In presence of more than ordinary amounts of P_2O_5 results are low unless molybdenum is correspondingly increased. In fact the proportion of all the other ingredients in the solution should be made to correspond to amount of P_2O_5 present. A good working proportion is this: 0.02 gram P_2O_5 , 15 grams NH_4NO_3 , volume 100 cc. and 30 cc. molybdate solution, containing 7 per cent free HNO_3 .

10. Chlorides

TABLE VI
Mg. of P_2O_5 found with

Chloride added Percentage	NaCl	NH_4Cl	$MgCl_2$	$CaCl_2$	$FeCl_3$	HCl (Sp. gr.) 1.20	$BaCl_2$
0	21.3	21.2	20.3	20.3	21.3	20.1	20.3
0.5	20.2	20.1	20.4	20.0
1	21.2	20.1	20.2	18.7	20.0	20.4
2	20.9	21.0	20.0	20.0	19.2	19.9	20.4
4	21.0	20.8	19.8	20.0	19.2	19.9	20.3
8	20.9	20.6	18.5	20.0	19.2	20.2
16	20.6	20.4

All chlorides examined tend to cause low results and solubility of yellow precipitate. Iron and magnesium chlorides are most injurious; calcium least. However, if HCl is used as the solvent in preparing the solution for analysis, then an aliquot is taken; the Cl present is not often sufficient to be perceptible in effect. The NH_4NO_3 used largely overcomes effect of Cl.

11. Nitrates

TABLE VII
Mg. P_2O_5 found with

Percentage added	HNO_3	$Cu(NO_3)_2$	$Fe(NO_3)_3$	$Mg(NO_3)_2$	$Ca(NO_3)_2$	$NaNO_3$	Added	NH_4NO_3
0	20.3	20.8	20.8	20.8	20.2	20.2	20.3
0.5	no pptn.	0	20.0
1	20.5	20.2	20.9	20.2	20.2	3	20.1
2	21.1	20.7	19.6	20.9	20.2	20.2	6	20.3
4	21.0	20.8	19.6	20.9	20.2	20.2	12	20.5
8	20.3	21.0	15.6	21.1	20.2	20.3	24	20.7
16	20.0	21.1	21.8	20.3	20.4	48	21.3

$NaNO_3$ in addition to regular NH_4NO_3 has little effect up to 5 per cent. But if substituted for NH_4NO_3 in part or whole the precipitate is soluble, more or less. Hence, it is best to avoid large amounts of sodium salts. Nitrates in small quantity tend toward high results, but in large amounts modify the character of the precipitate greatly and cause low results, like any soluble salt in large amount.

12. Sulfates

TABLE VIII
Mg. P_2O_5 found with

Percentage added	H_2SO_4	H_2SO_4 (NH_4NO_3 absent)	$(NH_4)_2SiO_3$	K_2SO_4	$CaSO_4$	$Fe_2(SO_4)_3$	$CuSO_4$	$HgSO_4$
0	20.3	20.1	20.8	20.8	21.0	21.0	21.0	21.0
0.5	21.1	20.5	21.5	20.3	21.9	21.4
1	21.2	20.3	21.4	21.5	21.5	19.8	21.8	21.4
2	21.1	19.8	21.5	21.4	21.6	11.4	21.9	21.5
4	20.9	18.1	21.3	21.3	21.5	21.9	21.1
8	18.5	21.0	21.2	21.9
16	17.4	20.0

In presence of soluble copper compounds, a little Cu is contained in the precipitate and causes the asbestos to appear green in final titration. When more than 2 per cent H_2SO_4 is present it shows a strong solvent action on the precipitate. In absence of NH_4NO_3 this is much more apparent. Up to 2 or 3 per cent, soluble sulfates in general cause high results, above 3 per cent usually causes low results, with the bad effects of excess of any soluble salts.

13. Removal of Soluble Sulfates from Solution

High results, due to soluble sulfates, are avoided by precipitating SO_4 by $BaCl_2$. This should always be done in presence of considerable free acid in order to prevent separation of barium phosphate. The solution is then diluted to a suitable volume and an aliquot taken for determination of P_2O_5 .

Examples of Removal of Sulfates

One hundred cc. phosphate solution placed in 200 cc. flask, added 5 grams K_2SO_4 , 6 cc. HNO_3 , boiled, added excess $BaCl_2$, neutralized with NH_3 , cooled, filled to mark, filtered, took for determination, 50 cc. = 0.0208 P_2O_5 found, 0.0209. This shows that P_2O_5 is not carried down by $BaSO_4$ in acid solution.

14. Examples of Effect of Soluble Sulfates

Solutions of various fertilizers made by digestion with H_2SO_4 and K_2SO_4 as if for determination of nitrogen; no $BaCl_2$ added to remove SO_4 : compared with solution of the same samples made by burning with MgO and dissolving in HCl, $BaCl_2$ added to remove SO_4 .

TABLE IX

Percentages P_2O_5 found with solution made by

Material	Burning with MgO	Digestion with H_2SO_4
No. 70. Complete fertilizer..	12.50 12.50	12.95 12.95 12.95
No. 78 Bone meal.....	22.30 22.30	21.85 22.45 22.70
No. 86 Tankage.....	12.55	13.20
No. 87. Complete fertilizer...	9.40	10.00

15. Soluble Silica

TABLE X— P_2O_5 FOUND WITH PERCENTAGE SiO_2 IN SOLUTION

0.0212	0.000
0.0212	0.005
0.0213	0.010
0.0218(a)	0.050
0.0217	0.100
0.0218	0.200

(a) After reprecipitating, this gave 0.0214.

If more than 0.05 per cent soluble SiO_2 was present it was precipitated by the acid phosphate solution before adding molybdenum, hence no higher results from larger amounts of SiO_2 present. The smaller amounts make the precipitate greenish yellow, flocculent, difficult to filter and very slow to dissolve in the KOH: results high. Reprecipitation removes most of the ill effects of soluble SiO_2 and brings result nearly correct.

16. Iron

Iron in solution as chloride, sulfate and nitrate causes low results, somewhat proportional to amount present (see Tables VI, VII, VIII). It always contaminates the yellow precipitate so that in final titration the end point is obscured by presence of ferric hydrate. This is somewhat prevented by presence of tartaric acid, or citric acid, in the molybdate solution, though enough tartaric acid to prevent separation of iron causes solubility of yellow precipitate and low results. Iron in the precipitate is avoided by double precipitation as given in E 18.

Low results due to iron may be largely avoided by use of a large excess of molybdate solution. In the solution containing 20.8 mg. P_2O_5 , presence of $FeCl_3 = 8$ per cent of Fe gave 13.2 mg. P_2O_5 when 30 cc. molybdate solution were used, but when 100 cc. molybdate were used, found 20.7 mg. P_2O_5 .

TABLE XI—EFFECT OF INCREASED MO IN PRESENCE OF MUCH FE

Molybdate used Cc.	Percentage Fe as $FeCl_3$	Mg. P_2O_5 found
30	0	20.8
30	4	19.2
75	4	20.7
30	8	13.2
100	8	20.7

17. Effect of Oxidizing Agents

Bromine, below 2 per cent, no effect apparent: large amounts cause low results.

Chromic acid acts much the same as H_2SO_4 , small amounts cause high results, large amounts, low results; 10 per cent completely prevented precipitation. A small amount of Cr was retained in the precipitate and gave a greenish tinge to final solution.

Potassium permanganate seems to cause somewhat high results, but this is uncertain because of the indefinite end point, especially with the larger amounts of $KMnO_4$, on account of the manganic oxide contained in the precipitate which masked the pink color in the final titration.

Results with these substances are shown in Table XII.

TABLE XII

Percentage substance added	Mg. P_2O_5 found with		
	$KMnO_4$	CrO_3	Bromine
0.0	20.1	20.1	20.1
0.1	20.1	20.4	20.0
0.5	20.3	20.5	20.0
1.0	20.4	20.1	20.1
2.0	20.5	19.7	19.8

18. Reprecipitation

In any case where the yellow precipitate is suspected of being impure, as from presence of MoO_3 , Fe, SiO_2 , or SO_4 , it may be purified and a more nearly correct result obtained by dissolving in NH_3 and reprecipitation provided that the whole of the P_2O_5 is contained in the first precipitate. After precipitation is complete, and precipitate well settled, pour off through the filter as much as possible of the supernatant liquid, retaining

precipitate in the flask. Add water and excess of NH_4OH to dissolve the precipitate in the flask, then HNO_3 till yellow precipitate begins to form, but keep a little alkaline. Now add 10 cc. NH_4NO_3 solution and water to make volume 100 cc., place in water bath at 65° , and when warm add 10 cc. molybdate solution with 5 cc. extra HNO_3 to re-form the yellow precipitate. After standing 15 minutes filter through original filter and treat as usual. The result is liable to be a little either high or low, but much better than if not reprecipitated. The slight amount of precipitate on the filter is not reprecipitated. The lack of exactness seems to be due to the difficulty in properly proportioning HNO_3 , NH_4NO_3 , Mo, and volume, as discussed in E 9. Too little NH_4NO_3 or Mo, too much H_2O or HNO_3 cause low results; too much NH_4NO_3 or Mo, too little HNO_3 or H_2O , or too high temperature cause high results.

TABLE XIII—EXAMPLES OF REPRECIPITATION

From pure Na_2HPO_4 Amount present.....	Mg. P_2O_5 found	
	Not reprecipitated	After reprecipitation
No injurious substance present....	20.1
1.5 grams $(NH_4)_2SO_4$	21.4	{ 19.9 20.2
Heated 1 hour at 65°	20.5	{ 20.0 20.3
Solution boiled.....	23.5	{ 20.1 20.5

Solution of fertilizer No.	Percentages P_2O_5 found	
	Not precipitated	After reprecipitation
19.....	33.5	33.4
20.....	26.3	26.5
23.....	15.2	15.4
24.....	28.7	28.8
26.....	7.6	7.8

19. Organic Impurities

Some are injurious in small amounts, while several per cent of others is scarcely noticeable. Proteid substances are usually very bad in effect, but this may be much diminished by boiling with HNO_3 . P_2O_5 in the acid soil extract, usually prepared for soil analysis, may well be determined without modification of the solution except when the soil contains much organic matter, when the latter must be decomposed by boiling with HNO_3 . The organic matter in an acid solution of steamed bone meal does not interfere much in the determination of P_2O_5 , but the solution from a tankage containing 5 per cent or more of N is not well suited for the determination. The organic matter in urine reduces the Mo, but after boiling with HNO_3 and HCl this difficulty is removed and P_2O_5 may be accurately determined in the solution without further treatment. Glue or gelatin forms an insoluble compound with the yellow precipitate, hence, is not admissible in the solution in which P_2O_5 is to be determined by the P. K. method. This fact is the basis of a titration method which has been worked out by A. Grete (G 41, 42) in which the boiling phosphate solution is titrated by a molybdate solution containing gelatin; the end point is that where no further precipitation occurs.

20. Precipitation by Shaking without Heating

Temperature used about 20° C., reagents, etc., same as in regular determination by heating, but time varied. Shaken by Wagner machine, same as used for determination of P_2O_5 in basic slag by Wagner citric acid method.

TABLE XIV—MG. P_2O_5 FOUND BY SHAKING METHOD

Solution contained.....	20.9	
Found after shaking 15 min.....	20.4	
Found after shaking 30 min.....	20.4	
Found after shaking 60 min.....	20.4	
Found, not shaken, 15 min.....	20.3	} Mixed and let stand at room temperature
Found, not shaken, 60 min.....	20.3	
Found, shaken 30 minutes.....	20.5	} Volume 200 cc. instead of 100 cc. Some MoO_3 pre- cipitated
Found, shaken 30 minutes.....	21.3	Used 100 cc. Mo instead of 30

Time shaken has little effect; standing without shaking gives same results as if shaken. Increased volume, increased molybdate, or decreased HNO_3 , cause separation of MoO_3 , same as if heating method were used.

21. Prevention of Separation of MoO_3 from Molybdate Solution on Heating

On account of the difficulty caused by separation of molybdic acid from the molybdate solution used in determining P_2O_5 , the following experiments were made with the hope of finding some feasible means of overcoming this defect in the method. So far nothing of the sort has been found, and these results are given to show what has been done, more for the guidance of any one who wishes to continue the investigation, than for the assistance of one who uses this method. Apparently the only way to avoid trouble from MoO_3 precipitated with ammonium phosphomolybdate is to avoid the conditions which cause it. These are discussed under headings *a*, *b*, *c*, etc.

a. Separation of MoO_3 from Solution by Heating with HNO_3

Solution contained MoO_3 about same as for ordinary determination, 1.65 grams $(NH_4)_2MoO_4$ in 100 cc., and varying NH_4NO_3 and HNO_3 , heated at 65° C. In absence of free HNO_3 , no separation of MoO_3 was caused by NH_4NO_3 from 0 to 15 per cent. When HNO_3 was added up to 1 per cent no MoO_3 was separated. From 2 to 10 per cent cause rapid separation of MoO_3 at 65°, most rapid with about 5 per cent HNO_3 . Above 10 per cent HNO_3 causes solubility of MoO_3 , and 16 per cent prevents separation entirely. With HNO_3 , but NH_4NO_3 absent, separation of MoO_3 was very slight. With 15 per cent NH_4NO_3 , 7 per cent HNO_3 and 3 per cent $(NH_4)_2SO_4$ there was no cloud after 2 hours' heating. This indicates that high results due to SO_4 are not because it tends to precipitate MoO_3 as had been supposed. Copper sulfate acted in the same way. $FeCl_3$, 2 per cent, delayed separation of MoO_3 for 45 minutes. $MgCl_2$, 10 per cent, and NH_4Cl , 10 per cent, had very little effect.

b. Effect of Ammonium Oxalate

TABLE XV

Time heated	Mg. P_2O_5 found
15 min. without oxalate.....	20.8 = correct amount
15 min. with 0.1 per cent oxalate.....	20.7
30 min. with 0.1 per cent oxalate.....	20.9
60 min. with 0.1 per cent oxalate.....	21.0

The oxalate has a solvent effect on yellow precipitate, also on MoO_3 , hence, results are lower in its presence and the high results usually obtained after long heating are not so high in its presence. But as oxalic acid is a solvent for both MoO_3 and the yellow precipitate, the result is not reliable for it is due merely to a lowering of the amount of MoO_3 which would be separated by long heating. The effect of long heating is to precipitate MoO_3 . This is partly balanced by the solvent effect of the oxalate and correctness of result is purely accidental.

c. Effect of Organic Matter

TABLE XVI—20.1 MG. P_2O_5 PRESENT

Reagent	Mg. P_2O_5 found	Reagent	Mg. P_2O_5 found
10 per cent alcohol.....	20.6	5 per cent cane sugar....	20.0
10 drops anilin.....	20.1	Glycerine, 4 per cent....	19.6
2 per cent anilin.....	19.6	Glycerine, 8 per cent....	19.5
10 per cent cane sugar....	19.9	Glycerine, 16 per cent....	15.4

Anilin causes reduction of molybdate solution, produces a blue color and interferes seriously. Sugar hinders separation of MoO_3 , also of yellow precipitate; hence, low results when much is used. Glycerine acts like sugar.

d. MoO_3 Precipitated by Heating Molybdate Reagent

Same solutions used as for regular P_2O_5 determination. 30 cc. molybdate and 15 grams NH_4NO_3 to 100 cc. total volume; heated at 65°, various time, filtered and titrated as usual, the MoO_3 being calculated as so much P_2O_5 .

TABLE XVII

Time heated	P_2O_5 equivalent of precipitate
15 min. gave.....	0.0000
30 min. gave.....	0.0008
60 min. gave.....	0.0046
120 min. gave.....	0.0140

This indicates that heating 15 minutes at 65° will not cause much error due to precipitated MoO_3 .

In another set of experiments solutions of same composition as above stated, were heated, one set 15 minutes, another set 60 minutes, filtered, washed and MoO_3 determined by three methods, titration with KOH ; titration with $KMnO_4$, after reduction by Zn ; and by drying and weighing. The amount separated by 15 minutes' heating was so small that duplicates did not agree well, but for 60 minutes' heating, results were fair.

TABLE XVIII

	Time heated	
	15 min.	60 min.
Mg. MoO_3 found by titration with KOH ...	6.6	88.8
Mg. MoO_3 found by titration with $KMnO_4$...	8.2	89.0
Mg. MoO_3 found by weight of precipitate..	4.2	93.7

Apparently the precipitate contains something else than MoO_3 as indicated by the higher result by weight after 60 minutes' heating. This may be $(NH_4)_2MoO_4$ or H_2MoO_4 , etc.

e. Solvents for MoO_3 and Yellow Precipitate

MoO_3 obtained by heating regular molybdate reagent on steam bath till most of the molybdic acid was precipitated: strength of reagents 10 per cent, unless otherwise stated. Cold H_2SO_4 , citric acid,

HCl, HCl and H_2O_2 , HCl and KMnO_4 , HCl and $(\text{NH}_4)_2\text{SO}_4$ give very slight effect. Warmed HCl or HNO_3 dissolved precipitates readily. Oxalic acid and ammonium oxalate dissolve precipitates readily. Na_2SO_3 decomposes, and reduces molybdenum. In general, both are acted on about alike, but yellow precipitate is somewhat more soluble than MoO_3 .

f. Prevention of Separation of MoO_3 on Heating Regular Molybdate Reagent Solution

Borax, sodium acetate, acetic acid, tartaric acid, alcohol, ether, toluol, phenol, CCl_4 , no effect. H_2O_2 , KMnO_4 , CrO_3 , iodine, 4 per cent glycerine, 10 per cent cane sugar, prevent separation of MoO_3 .

22. Effort to Improve End Point

One weakness of the volumetric method is the lack of sharpness of the end point in the final titration. This is due to (a) phosphoric and molybdic acids being polybasic, and to their tendency to form two or more salts with the same base at the same time; and (b) the solution contains NH_3 for which phenolphthalein is not the best indicator. The latter is not of enough importance to merit much attention as ammonia may fairly well be titrated with this indicator provided it is dilute and cool as shown by Thomson (G 15). However, ammonia may be removed by boiling with excess of the standard fixed alkali, before titrating back with standard acid. This is the basis of Neumann's variation of the method (G 14).

b. The difficulty with polybasic phosphoric acid is avoided by removing it by means of neutral BaCl_2 , thus leaving HCl in the solution for final titration. It was hoped that a similar plan could be followed with molybdic acid, but this did not succeed, although molybdic acid is precipitated by BaCl_2 . After addition of BaCl_2 , the end point was no sharper, in fact, was obscured by the large amount of white precipitate formed in the solution. Lead nitrate precipitates both phosphoric and molybdic acids. This was followed by excess of sodium sulfate to remove Pb. After this the end point was still less distinct, in presence of the large amount of white precipitates. Further efforts included, at various times, addition of sugar, glycerine, alcohol, ether, none of which was of any assistance. Among other indicators tried, rosolic acid was the only one at all suitable and it is not as good as phenolphthalein.

23. Determination of Phosphoric Acid Equivalent of the Standard Alkali Used in the Volumetric Method

One essential to the success of the volumetric method is that the strength of the standard alkali be accurately known in terms of P_2O_5 . In theory this may be satisfactorily done by calculation from the equation $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{12} + 23\text{KOH} = (\text{NH}_4)_2\text{HPO}_4 + 11\text{K}_2\text{MoO}_4 + 11\text{H}_2\text{O} + \text{NH}_4\text{KMoO}_4$. But as this equation and the exact composition of the yellow precipitate are matters of theory upon which all authorities do not agree, it seems best to depend on setting a standard by analysis of a compound of known P_2O_5 content. Many such have been proposed, and none of them are really satisfactory. The water-soluble crystalline phosphates

contain water of crystallization, the amount of which is usually uncertain; hence their unreliability. Most of the insoluble phosphates are very difficult to prepare in a pure state, as they cannot be purified by recrystallization, and many of them are partly hydrolyzed by washing with water, so that their exact composition is not certain. My efforts to prepare BaHPO_4 , CaHPO_4 , PbHPO_4 , BiPO_4 , etc., did not succeed in making salts of constant composition. Silver phosphate was used as basis of atomic weight determinations by Baxter and Jones (G 32) and was prepared by them of perfectly definite composition. Dumas used it as a basis for standardizing the gravimetric method of P_2O_5 determination (G 31). In my experience the chief trouble with it is to prepare it in a pure state. This requires conditions which the ordinary laboratory does not possess, *e. g.*, a dark room and an abundance of sufficiently pure water. It is difficult to dry without reduction of the silver, but this does not seem to make much difference in the ratio of Ag to PO_4 . I made several preparations of Ag_3PO_4 . One was analyzed with the following results: Ag weighed as AgCl , P weighed as $\text{Mg}_2\text{P}_2\text{O}_7$.

		Found	Theory for Ag_3PO_4
Ag_2O	83.04	83.06	83.03
P_2O_5	16.96	17.01	16.97

This sample was used to set the strength of the standard alkali, NaOH.

Besides this, many comparisons of results by both gravimetric and volumetric methods on fertilizers, etc., have been made, and accuracy of the volumetric method thus established. For the purpose of this study a solution of 3 grams sodium phosphate in one liter of water was used. The phosphate was not recrystallized and had lost some of its water of crystallization, so that the P_2O_5 in it was not always the same in the numerous solutions that were used during the more than two years of investigation. In one of these solutions was found:

	Mg. P_2O_5
By gravimetric method using 50 cc.....	40.7
By gravimetric method using 50 cc.....	40.7
By volumetric method using 25 cc.....	20.3
By volumetric method using 25 cc.....	20.4
} = 40.7	

Assuming the formula of the yellow precipitate to be $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{12}$ it would contain 3.78 per cent P_2O_5 . The precipitate is easily dried and weighed, and using this factor P_2O_5 is found thus gravimetrically. Many have used this method successfully. My work with it has been little, but indicates that it is about as reliable as the volumetric method and in general subject to the same sources of error, the chief of which is due to contamination with molybdic acid. A few results are given.

TABLE XIX

P_2O_5 found by multiplying weight of yellow precipitate by 0.0378.
Mg. P_2O_5 in solution used, 21.1

Time heated in precipitating at 65° C.	Mg. yellow precipitate	Mg. P_2O_5
15 min.	565.5×0.0378	= 21.4
	566.5	= 21.4
60 min.	585.4	= 22.1
	587.9	= 22.2

The last illustrates the effect of long heating to precipitate MoO_3 .

24. Methods of Making Solutions of Phosphates

The following methods of making the solution are used:

- Dissolve in water.
- Dissolve in HCl , HNO_3 or both.
- If organic matter is present it may be removed by ignition either alone or with MgO or MgNO_3 or both, then dissolved in acid; or by wet combustion as in the Kjeldahl method for nitrogen; or sometimes by boiling with HNO_3 .

Ignition with Magnesia.—This method is applicable to almost any organic material and the solution thus prepared is suitable for analysis by either the gravimetric or volumetric methods. It is the method mostly used in this laboratory. In a platinum or porcelain dish of 20–30 cc. capacity, place a layer of MgO , 2–3 mm. thick. On this place the sample, 2 grams mixed with an equal bulk of MgO . Cover the whole with a little MgO . If the substance is a liquid it may be mixed with MgO , and dried before ignition. Place in the muffle furnace, which should be cold. The muffle will heat so gradually that there is no danger of loss of the substance. It should finally be heated to bright red. If necessary to use a flame for the ignition, start with a very small flame and in course of 15–30 minutes increase to bright red. After cooling, wash contents of the dish into a flask (200, 250, or 500 cc. capacity) with water, add 20–30 cc. HCl and heat to boiling a few minutes. Be sure that there is an excess of acid present. When all is dissolved that is soluble, remove flask from the heat and at once add solution of BaCl_2 sufficient to throw down all soluble sulfates. Cool, fill to mark, mix. The solution may be filtered, or the flask allowed to stand a few hours, when the clear solution may be pipetted out, without filtering, for the analysis.

I have used this method for five years and found it very satisfactory. A similar plan was recently proposed (G 38). Although I have not experimented much on this point, my work indicates that some phosphorus may be lost from volatile organic substances containing it when ignited with magnesia. Presence of $\text{Mg}(\text{NO}_3)_2$ guards against this loss. About 5 cc. of the official solution is mixed with the sample in a platinum dish, then some MgO added, the whole dried, then ignited as above. The MgO prevents loss of substance by deflagration which occurs when organic matter is ignited with $\text{Mg}(\text{NO}_3)_2$ in absence of added MgO . Avoid excess of Mg as it tends to cause low results (see Table VI).

25. Use of HCl or H_2SO_4 , etc., instead of HNO_3 for Acidifying Ammonium Molybdate Solution

To 30 cc. neutral ammonium molybdate, of same strength as used for regular P_2O_5 determination, added 10 grams NH_4Cl , 2 cc. HCl and water to make total volume 100 cc. After a few minutes a flocculent precipitate formed and dissolved on heating at 65°C .; after 10 minutes precipitate formed again and would not dissolve by boiling. Dissolved in excess of NH_3

acidified with HCl it formed a clear solution which gradually became cloudy on standing at 65° , by separation of MoO_3 much the same as if the usual molybdate solution made up with nitrates instead of chlorides, were used. When the experiment was repeated, but using 4 cc. HCl instead of 2 cc. as at first, the precipitate did not form so soon, but otherwise acted about the same. Hence, it is inferred that HCl and its salts do not serve well instead of HNO_3 and its salts to make the molybdate solution for determination of P_2O_5 , although MoO_3 does not separate as quickly from this solution as from the nitrate solution.

When this chloride solution of MoO_3 was used to determine P_2O_5 the usual yellow precipitate was formed, but not so well as if the nitrate solution were used. Substituting H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ in the molybdate solution instead of nitrate gave similar effects, but better than with chlorides. When acetic acid was used there was no precipitate formed, hence, it is unable to take the place of nitric acid. A certain amount of free acid is necessary to cause formation of the yellow precipitate. In these experiments it was observed that a larger volume of HNO_3 than H_2SO_4 is needed, and more HCl than HNO_3 , which is to be expected, considering the relative amount of acid in a given volume of each.

TABLE XX.— Mg , P_2O_5 FOUND BY USE OF HCl , H_2SO_4 , $\text{C}_2\text{H}_5\text{OOH}$ INSTEAD OF HNO_3 IN MOLYBDATE SOLUTION

Cc. acid	HCl	H_2SO_4	Acetic acid
1.....	13.5	22.1	No precipitate
2.....	6.0	21.8
4.....	21.7	21.6
P_2O_5 present.	21.0	21.0

26. Composition of the Yellow Precipitate

Many investigators have analyzed ammonium phosphomolybdate, and with somewhat various results, though it is ordinarily accepted that its formula is $(\text{NH}_4)_3\text{PO}_4(\text{MoO}_3)_{12}$. My work indicates that the most probable cause of variable results is the contamination of the yellow precipitate with MoO_3 or other compounds of molybdenum, most frequently caused by too high temperature or too long heating at moderate temperature. When the precipitate, formed in a not too concentrated solution at high temperature, is examined by the microscope it is found to contain two very distinct kinds of crystals, the yellow rhombohedrons of ammonium phosphomolybdate often united into beautiful stars, and long, slender, colorless needles of molybdic acid. A number of different preparations of the yellow precipitate made under conditions known to favor separation of MoO_3 were found by the microscope to contain crystals of MoO_3 while if these conditions were avoided the MoO_3 could not be seen. All my efforts to separate the two compounds after they are formed together were unsuccessful, as indicated in 21. My theory is that the yellow precipitate is as definite in composition as BaSO_4 or AgCl , even though formed under very different conditions of precipitation. This was stated by Hundeshagen in 1888.¹ The following experiments are given to support this theory. The fact that avoidance of conditions known to cause separation of MoO_3 in actual analytical

¹ Z. anal. Chem., 26, 141.

work leads to correct results, while the opposite is nearly sure to cause incorrect results, is also in support of this theory.

A quantity of yellow precipitate was made, well washed and dried at 120° C. Portions of this were dissolved and reprecipitated under various conditions as given below, filtered, washed and dried as before. From these, and also from the original, portions of 0.5 gram were weighed out and titrated with KOH as if for a regular determination. Uniformity of the results, as shown by constant acidity, indicates that the precipitate is of definite and constant composition even though formed under quite varied conditions.

TABLE XXI

Conditions of reprecipitation	KOH used Cc.
15 min. at 65°	18.6
60 min. at 65°	18.6
15 min. at 65° and 3 per cent (NH ₄) ₂ SO ₄	18.5
15 min. at 65° and 10 per cent MgCl ₂	18.5
15 min. at 65° and 1 per cent FeCl ₃	18.5
Boiled	18.7
Original preparation	18.6
Original preparation	18.6

The reprecipitation was effected by HNO₃, no more MoO₃ being added, hence the MoO₃ usually separated by adverse conditions, from the usual excess present, did not appear, but in each case precipitation was incomplete as shown by formation of more yellow precipitate on addition of molybdate solution to the filtrate. (This illustrates the need of an excess of Mo in order to secure complete separation of P₂O₅.)

F. SUMMARY

Working details of the Pemberton-Kilgore method for determination of phosphoric acid are given.

Great rapidity and fair accuracy of the method are shown.

A satisfactory method of preparing asbestos for filtration is given. In the detailed study of conditions affecting the method it is shown that:

High temperature causes high results; too low temperature causes low results; but in both cases this is much modified by time. Below about 40° C., temperature has not much effect, regardless of time: higher temperature than this is desirable in order to secure a desirable quality of precipitate. The longer the precipitate is heated and the higher the temperature the higher the result: 15 minutes at 65° gives best results (E 1 and 2).

In too concentrated solution precipitate is finely divided and difficult to filter. In too dilute solution separation is incomplete in reasonable time. A suitable concentration is 20 mg. P₂O₅ in 100 cc. (E 3).

Too little molybdate solution gives low results; too much tends to high results, due to its tendency to separate MoO₃ on heating (E 4).

Nitric acid is necessary to the reaction but too much causes solubility of precipitate (E 5).

This is counteracted by ammonium nitrate which tends to precipitate MoO₃ (E 6). Hence, HNO₃ and NH₄NO₃ should be properly proportioned as shown in E 9. Volume, P₂O₅, and molybdate solution must also be considered here.

Chlorides, in general, cause solubility of yellow pre-

cipitate and low results, partially avoided by use of NH₄NO₃ (E 10).

Nitrates in general cause high results, by causing separation of MoO₃ (E 11).

Sulfates cause high results (E 12), remedied by reprecipitation (E 18).

Soluble silica in small amount is negligible; in larger amount, causes high results (E 15), avoided by reprecipitation (E 18).

Iron tends to cause low results, remedied by larger excess of molybdate solution (E 16).

Oxidizing agents as such have no specific effect (E 17).

When the yellow precipitate is contaminated from any cause, it may be purified and made nearly correct by reprecipitation (E 18).

Organic matter tends to cause low results and difficulty in manipulation (E 19), hence, should be removed by burning (E 24c).

Shaking in cold instead of heating to form yellow precipitate tends to low results, is of no advantage to avoid separation of MoO₃, and is not so convenient as the method using heat (E 20).

There is no suitable method to avoid high results caused by MoO₃ separated with the yellow precipitate except reprecipitation. It is much better to avoid its separation in first place (E 21).

Effort to improve end point of titration failed (E 22).

Ag₃PO₄ is a suitable substance for setting the strength of the volumetric solution used (E 23).

A simple and convenient method of removing organic matter by ignition with MgO is explained (E 24).

The idea that some other than the nitrate solution of MoO₃ may be used for precipitating P₂O₅ is found erroneous. It was thought that separation of MoO₃ would be less in some other than the nitrate solution (E 25).

Variable composition of the yellow precipitate as indicated in the literature is probably due to MoO₃ separated with it but not in any proper sense a part of the yellow precipitate (E 26).

G. BIBLIOGRAPHY

1. Pemberton's Original Method. J. Am. Chem. Soc., **15**, 382 (1893). Also in Chemical News, **46**, 4.
2. Pemberton's Later Method. J. Am. Chem. Soc., **16**, 278 (1894).
3. Kilgore's Method. U. S. D. A., Division of Chemistry, Bulletin **43**, 68-104 (1894).
4. Work on Kilgore's Method by A. O. A. C. U. S. D. A., Bureau of Chemistry, Bulletin **47**, 70 (1896); **49**, 60 (1897); **56**, 76 (1899); **57**, 69 (1899); **62**, 35 (1901); **67**, 22 (1902); **81**, 164 (1904).
5. Kilgore's Work on Proper Washing of Yellow Precipitate. Use 200 cc. H₂O, Wash by Suction. J. Am. Chem. Soc. **19**, 703 (1897).
6. Time to Separate Yellow Precipitate. De Roode. J. Am. Chem. Soc., **17**, 43 (1895).
7. Williams Shaking Method. J. Am. Chem. Soc., **23**, 8 (1901). With description of filter tube, etc., as used in California Fertilizer Control.
8. Investigation of Pemberton-Kilgore Volumetric Method by Veitch. J. Am. Chem. Soc., **18**, 389 (1896).
9. Determination of P₂O₅ in Presence of Colloidal Silica; Washing with H₂O₂, etc. Chem. Abstracts, **6**, 1416 (1912), June 10. From Compt. rend., **154**, 775.
10. Removal of Soluble Silica Precipitated with Yellow Precipitate by Washing with Water. Z. anal. Chem., **26**, 584.
11. Solubility of MoO₃ and Yellow Precipitate in Washing Solutions. U. S. D. A., Bureau of Chemistry, Bulletin **47**, 72-73. Same subject in Z. anal. Chem., **3**, 446. (1864).

12. Effect of Soluble Sulfates. Richardson, J. Am. Chem. Soc., 1314 (1907).
13. Use of Tartaric Acid to Prevent Separation of Fe and Mo, by Juptner, Chem. Centralblatt, 2, 1813 (1894).
14. Neumann's Method. Z. phys. Chem., **37**, 115 (1902). (Boils yellow precipitate with KOH to remove NH₃, then cools and titrates back with acid.)
15. Reaction of Phenolphthalein with P₂O₅. Thompson, Chemical News, **47**, 127, 186 (1883).
16. Amount of Phenolphthalein Necessary to Use. Long, Am. Chem. J., **11**, 84 (1889).
17. Direct Weighing of Yellow Precipitate. Gladding, J. Am. Chem. Soc., **18**, 23 (1896); U. S. D. A., Div. of Chemistry, Bulletin **61**, 47 (1898); **49**, 60 (1897).
18. Purification of Yellow Precipitate by Double Precipitation and Estimation of P₂O₅ by Weight of Yellow Precipitate, with Study of Effect of Iron and Various Substances. Woy, Chem. Ztg., **21**, 442 (1897). Translation in Treadwell & Hall, Anal. Chem., II, 344.
19. Finkner's Method. Berichte, **11**, 1640 (1878). Well washed and dried at 160-180, factor, 0.3794. Hundeshagen's factor for same is 0.3753.
20. Estimation of P₂O₅ by Weight of Yellow Precipitate, Wash with Acetone Dry in Vac. Lorenz method, Chem. Abstracts, May 20, 1912, 1266. Original in Z. anal. Chem., **51**, 161-175. First paper *Ibid.*, **46**, 193.
21. Estimation of P₂O₅ by Weight of Yellow Precipitate. Chem. Abstr., **6**, 584 (1912), March 10. Original in Oesterr. Chem. Ztschr., **14**, 1-5 and abstract in J. Chem. Soc., **100-11**, II, 1028.
22. Lorenz Method Direct Weighing of Yellow Precipitate after Drying. Landw. Vers.-Stat., **55**, 183.
23. Ignition of Yellow Precipitate to P₂O₅ (MoO₃)₂, Effect of Various Salts and Adding Mo Solution Gradually. Sherman & Hyde, J. Am. Chem. Soc., **22**, 652 (1900).
24. This is essentially Woy's method. Chem. Ztg., **21**, 441, 469 (1897).
25. Precipitate Ignited below Red Heat and Weighed. Factor = 0.3946 for P₂O₅ (MoO₃)₂. Berichte, **11**, 1640 (1878).
26. Estimation of P₂O₅ by Weight of Yellow Precipitate, after Heating till Blue. Factor, 0.0396. Double Precipitation Used to Get Pure Precipitate. Auld, Analyst, **37**, 130 (1912).
27. Use of BaCl₂ to Get Correct End Point in Titration. THIS JOURNAL, July, 1912, p. 520.
28. Volumetric Determination of P₂O₅, Use of BaCl₂, to Improve End Point. Chem. Abstr., May 20, 1912, p. 1265. Original in J. Wash. Acad. Sci., **2**, p. 114.
29. Colorimetric Determination of P₂O₅. Chem. Abstracts, March 10, 1912, p. 662.
30. Colorimetric Determination of P₂O₅. Prep. Sodium Molybdate, Etc. Expt. Station Record, **26**, 406 (1912, April).
31. Silver Phosphate as Standard for P₂O₅. Dumas, Chem. Eng., **11**, 185 (1910).
32. Preparation of Pure Ag₃PO₄. Baxter and Jones, J. Am. Chem. Soc., **32**, 298 (1910).
33. NaNH₄HPO₄·H₂O as Standard Phosphate. Jorgensen, Z. anal. Chem., **45**, 273 (1906).
34. Hundeshagen's Work on Yellow Precipitate, Etc. Z. anal. Chem., **28**, 141. Trans. in Chemical News, **60**, 168, 177, 188, 201, 215.
35. Comparison of Several Methods for P₂O₅ Determination by D. J. Hissink. Chem. Weekblad, **115**, (1905).
36. Influence of Al, Mg, Ca on P₂O₅ Determination. Neubauer, Landw. Vers.-Stat., **63**, 141 (1905-6).
37. Citric Acid to Prevent Contamination of MgNH₄PO₄ with MgO. Lorenz, Z. anal. Chem., **32**, 64 (1893).
38. Use of MgO for Incinerating Material for P₂O₅ Determination. Chem. Abstracts, **6**, 1416 (1912, June). From Z. physiol. Chem., **76**, 426.
39. Same subject in Experiment Station Record, **28**, 20 (1913, Jan.).
40. Loss of P₂O₅ in Burning Wheat. Leavitt and LeClerc, J. Am. Chem. Soc., **30**, 391, 617 (1908).
41. Direct Titration of Phosphate Solution by Molybdate Solution Containing Gelatin. By A. Grete, in Koenig's Unters. Landw. und Gewerblich. Stoff.
42. Same subject in Experiment Station Record, [3] **28**, 203 (1913).
43. Neumann's Method for P₂O₅, Use of Formaldehyde. Experiment Station Record, **26**, 406 (1912, April).
44. Loss of Phosphorus on Ignition of Mg₂P₂O₇. Neubauer, J. Am. Chem. Soc., **16**, 289 (1894).
45. Composition of Yellow Precipitate, Etc. By Baxter, Am. Chem. J., **28**, 298 (1902).
46. Same by Baxter and Griffin, Am. Chem. J., **34**, 204 (1905).
47. Use of H₂SO₄ to Obtain Constant Results. By Lagers, Z. anal. Chem., **47**, 561 (1908).

FERTILIZER CONTROL LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

THE COMPOSITION OF SEDIMENTS FROM THE POTOMAC AND SHENANDOAH RIVERS

By JOSEPH G. SMITH AND WILLIAM H. FRY¹

Received October 13, 1913

This investigation was undertaken to ascertain whether or not the sediments from the two rivers showed any marked chemical and mineralogical differences, with a view to using the results in the study of soil erosion. Samples of water were collected by the Weather Bureau in five-gallon lots, at various times during an interval of two years. The sediments were allowed to settle, the water siphoned off and the residues dried. In most cases the amount of sediment was so small that a chemical analysis was impossible. Mineralogical examinations, however, were made of each sample. The particles, generally, were of extremely small size; and were very much weathered and coated with iron oxides, hydroxides, organic matter, and possibly other material. Consequently, the character of the larger percentage of the grains was wholly indeterminable. The mineralogical analyses represent simply that part of the material which was in large enough particles and fresh enough for determination. This determinable matter probably never amounted to more than ten per cent of the total sample. It is not to be concluded that the minerals cited in the following tables were the only ones present. They are the more prominent ones which could be positively identified, and it is quite probable that other mineral species were present which defied identification.

The lithology of the two river basins seems to be very similar as will be seen from the following résumé:

The Potomac River above Cumberland comes into contact with sandstones, shales, limestones, etc. From Cumberland to Harper's Ferry it flows over or in close proximity to sandstones, shales, limestone, and unconsolidated sands and clays.²

The Shenandoah River above Riverton flows over limestone-shale and sandstone-shale formations. The headwaters rise in a sandstone-shale-limestone formation, and flow over a narrow band of sandstone-shale. Below Riverton it flows over limestone and shale, and touches a sandstone-shale-quartzite formation.³

DETAILED MINERALOGICAL ANALYSES (W. H. FRY, ANALYST) SEDIMENTS FROM CUMBERLAND, MD. (POTOMAC RIVER)

No. 1. Hornblende, biotite, quartz, feldspar [labradorite(?)], orthoclase. The doubtful labradorite showed twin structure and the determination was made by the extinction of the twins in conjunction with the refractive index. However, the particle was very small; but it is certainly one of the plagioclase group. There were present very small fragments of what appear to be silicious tests of spicules of some form of microscopic animal or plant life.

No. 2. Quartz, biotite, animal or vegetal spicules, plagioclase, a doubly refracting grain with a high index of refraction which may be zircon (the small size of the particle prohibited its determination), hornblende(?), small amount of magnetic particles.

No. 3. One rather large grain of what appears to be a glass. It is isotropic with an index or refraction very near 1.54. It is probable that this is a fragment broken from a glass vessel. Magnetic particles, quartz, hornblende.

No. 4. Magnetic particles, muscovite, quartz, isotropic particles with index of refraction near 1.54, plagioclase.

No. 5. Largely organic matter. The organic material masks the mineral constituents so as to make them indeterminable.

¹ Scientists in Soil Laboratory Investigations, Bureau of Soils, U. S. Department of Agriculture.

² Maryland Geological Survey, **3**, Pl. 6 (1899).

³ T. L. Watson, "A Geological Map of Virginia," Va. Geol. Survey.

No. 6. Quartz, some indeterminate ferromagnesian mineral, hornblende, animal or vegetable tests.

No. 7. Muscovite, biotite, quartz, animal or vegetable tests, hornblende.

No. 21. Magnetic particles, quartz, muscovite, plagioclase, animal or vegetable tests, biotite, microcline.

No. 29. Magnetic particles, quartz, muscovite, hornblende, biotite, animal or vegetable tests, orthoclase.

No. 41. Quartz, hornblende, biotite. All of the particles in this sample are of very small dimensions.

No. 36. Slight amount of magnetic particles, quartz, orthoclase, hornblende, mica(?).

No. 39. Magnetic particles, quartz, muscovite, biotite, hornblende, animal or vegetable tests.

No. 41. Magnetic particles, quartz, hornblende, muscovite, orthoclase, biotite. Very much vegetable matter present.

No. 43. Slight amount of magnetic particles, quartz, biotite, hornblende.

SEDIMENTS FROM RIVERTON, VA. (SHENANDOAH RIVER)

No. 14. Quartz, garnet, muscovite, biotite, orthoclase.

No. 15. Magnetic particles, quartz, biotite, orthoclase.

No. 16. Quartz, muscovite, animal or vegetable tests, biotite.

No. 20. Quartz, muscovite, biotite, plagioclase (?), garnet, hornblende.

No. 27. Quartz, plagioclase. This material is extremely fine and is very much coagulated.

No. 31. Slight amount of magnetic particles, quartz, biotite, orthoclase, hornblende.

No. 32. Isotropic particles with index of refraction about 1.54, probably glass, quartz, orthoclase, biotite, hornblende.

No. 37. Quartz, calcite. This material is extremely fine.

No. 38. Quartz, hornblende, mica(?). Material is very fine.

SEDIMENTS FROM HARPER'S FERRY (POTOMAC RIVER)

No. 8. Quartz, biotite, muscovite, labradorite, orthoclase, few vegetable or animal tests, chlorite(?).

No. 9. Quartz, hornblende, biotite, plagioclase, muscovite.

No. 10. Quartz, muscovite, particles deeply coated and impregnated with some coloring matter, probably iron oxides.

No. 11. Magnetic particles, quartz, hornblende, muscovite, animal or vegetable spicules, biotite, plagioclase.

No. 12. Magnetic particles, quartz, zircon, hornblende, calcite plentiful, tourmaline, biotite, orthoclase, muscovite.

No. 13. Magnetic particles, quartz, very much altered biotite, plagioclase, hornblende, muscovite.

No. 18. Magnetic particles, quartz, muscovite, garnet, biotite, orthoclase.

No. 19. Magnetic particles, quartz, biotite, garnet, hornblende, plagioclase, orthoclase.

No. 22. Magnetic particles, quartz, biotite, muscovite, microcline, plagioclase, orthoclase, hornblende. A fair amount of this material consists of grains of about the dimension of very fine sands, thus differing from the usual silty or clayey character of the sediments. These large grains are mainly quartz.

No. 23. Very small amount of magnetic particles, quartz, biotite, small amount of animal or vegetable tests, labradorite, some ferromagnesian mineral, muscovite, orthoclase. Practically all the particles are very small.

No. 24. Quartz, animal or vegetable tests, microcline, labradorite, biotite, muscovite, orthoclase, hornblende, calcite.

No. 25. Small amount of magnetic particles, quartz, plagioclase, biotite, muscovite, hornblende, orthoclase.

No. 26. Magnetic particles, quartz, muscovite, tourmaline, orthoclase, plagioclase, biotite, hornblende.

No. 28. Quartz, biotite, animal or vegetable tests, rutile, garnet, muscovite, hornblende.

No. 30. Very slight amount of magnetic particles, quartz, biotite, orthoclase, plagioclase, rutile, microcline, muscovite, shell fragments which effervesce with hydrochloric acid.

No. 33. Very slight amount of magnetic particles, quartz, muscovite, hornblende, biotite.

No. 35. Very slight amount of magnetic particles, quartz, hornblende, biotite, orthoclase, plagioclase(?), muscovite.

No. 40. Quartz, orthoclase, biotite, hornblende, muscovite, plagioclase.

No. 42. Magnetic particles, quartz, microcline, biotite, muscovite, calcite, plagioclase.

No. 44. Magnetic particles, quartz, labradorite, biotite, muscovite, orthoclase.

No. 45. Small amount of magnetic particles, quartz, muscovite, biotite, hornblende.

No. 46. Small amount of magnetic particles, quartz, hornblende, some mineral which appears to be an amphibole other than hornblende, muscovite, biotite.

No. 47. Magnetic particles, quartz, hornblende, muscovite, plagioclase, biotite.

No. 48. Quartz, muscovite, biotite(?), calcite(?).

No. 49. Quartz, hornblende. Particles extremely fine.

TABLE I—SUMMARY OF THE MINERALS FOUND IN THE SEDIMENTS FROM THE DIFFERENT STATIONS

CUMBERLAND	RIVERTON	HARPER'S FERRY
Hornblende	Hornblende	Hornblende
Biotite	Biotite	Biotite
Quartz	Quartz	Quartz
Orthoclase	Orthoclase	Orthoclase
Plagioclase	Plagioclase	Plagioclase
Magnetite	Magnetite	Magnetite
Muscovite	Muscovite	Muscovite
Labradorite(?)	Labradorite
Zircon(?)	Zircon
Microcline	Microcline
Femic mineral(?)	Femic mineral(?)
.....	Garnet	Garnet
.....	Calcite	Calcite
.....	Tourmaline
.....	Rutile
.....	Chlorite(?)

As can be seen from Table I, the sediments from Riverton do not show the presence of microcline, the doubtful femic mineral, labradorite, and zircon which are present in the sediments from Cumberland, while the Riverton sediments contain garnet and calcite in addition to the minerals found in the Cumberland sediments. The sediments from Harper's Ferry, where the two rivers join, contain all of the minerals found in the sediments from the other two stations, and tourmaline, rutile, and doubtful chlorite in addition. However, it should be remembered that only a relatively small proportion of the minerals were determinable and that the composition of the indeterminate material, were it known, might or might not considerably modify this table.

TABLE II—CHEMICAL ANALYSES OF SEDIMENTS FROM CUMBERLAND
C. F. Miller, Analyst

No.	SiO ₂	Al ₂ O ₃ + Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	Na ₂ O	K ₂ O
1	52.03	27.78	0.65	1.70	0.30	1.92	3.28
6	48.97	24.88	1.15	1.16	0.40	1.41	2.36
34	55.23	25.50	1.07	1.37	0.24	0.67	2.91

TABLE III—CHEMICAL ANALYSES OF SEDIMENTS FROM RIVERTON
R. F. Gardiner, Analyst

No.	SiO ₂	Al ₂ O ₃ + Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	Na ₂ O	K ₂ O
14	63.00	22.56	0.48	0.90	0.52	0.72	1.36
27	67.07	21.06	0.46	1.12	0.34	0.90	2.42
38	50.51	27.34	0.63	1.27	0.63

TABLE IV—CHEMICAL ANALYSES OF SEDIMENTS FROM HARPER'S FERRY
Average of Duplicate Analyses by R. F. Gardiner and C. F. Miller

No.	SiO ₂	Al ₂ O ₃ + Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	Na ₂ O	K ₂ O
12	58.91	22.70	1.33	0.94	0.43	0.76	1.93
22	67.05	18.05	0.50	0.91	0.46
23	63.33	20.95	0.71	1.00	0.30	1.70	2.18
28	64.73	20.54	0.86	1.07	0.28	0.78	2.26
35	62.53	21.08	1.12	1.23	0.29	0.48	2.05
48	53.73	25.00	1.07	1.44	0.31	0.90	2.16

The soda and potash determinations were made by the J. Lawrence Smith method, the others by fusion with sodium carbonate. Samples 22 from Harper's Ferry and 38 from Riverton were so small that only a partial analysis could be reliably made.

The analyses do not show any definite relation between chemical composition and the amount of sediment carried in the streams when the samples of water were taken. This was to be expected, since unequal rainfall over the varying geological formations of these large river basins would carry into the streams material of varying composition.

The results are in harmony with the well-known

fact that the finer particles of soils such as would be carried by stream waters are high in potash, phosphoric acid, lime, organic matter, etc.

BUREAU OF SOILS
U. S. DEPT. AGRIC., WASHINGTON

ESTIMATION OF THE LIME REQUIREMENT OF SOILS¹

By J. A. BIZZELL AND T. L. LYON

Several methods have been proposed for the estimation of soil acidity, but none is entirely satisfactory. The difficulty is that the true nature of the acidity is not understood. The problem is further complicated by the fact that lime may be beneficial to a soil in other ways than by simply correcting an acid condition. The nearest approach to a quantitative determination of the lime requirement of a soil, therefore, would seem to be an estimation of the total absorptive power of that soil for lime. This is the principle upon which the well-known method proposed by Veitch² is based. The most serious objection to this method from the analyst's standpoint is the large number of determinations which must frequently be made before the alkaline point is reached. The writers have also frequently found it difficult and sometimes almost impossible to determine the saturation point. This is true particularly of soils containing a large quantity of organic matter yielding highly colored extracts, and of those containing a large percentage of clay. Many clay soils will not settle sufficiently, even after very long standing, and the clay particles in such cases are so fine as to defy filtration by the ordinary methods.

With a view to overcoming these difficulties the writers have examined a method described by R. Albert³ and propose certain modifications which seem to render it suitable for estimating the lime requirement of soils.

In brief, the method as proposed by Albert is as follows: To 25 grams of air-dried soil add 200 cc. boiled distilled water, 50 cc. of a standard solution of barium hydroxide, and 5 grams solid ammonium chloride. Distill the mixture, collecting the ammonia formed in tenth-normal acid. The amount of ammonia found in the distillate is assumed to be proportional to the free barium hydroxide not required to saturate the soil. Barium hydroxide was found

This method was compared with the Veitch method on a number of samples of soil and subsoil of the Dunkirk clay loam type, obtained from the experiment field. The results are given in Table I.

The results by the two methods were widely different, and in view of the field results obtained by the use of lime on this soil, indicated that the figures obtained by the Albert method were much too low. This discrepancy appears to be due chiefly to two factors which apparently were not recognized by the author.

In the first place solid ammonium chloride undergoes slight decomposition when boiled with water, and appreciable quantities of ammonia are given off. When boiled with some soils ammonium chloride gives up enough ammonia to very materially affect the results, rendering the figures for acidity much too low. The amount of ammonia given off was different for each soil. Twenty-five samples were examined and the ammonia formed expressed in equivalent of tenth-normal acid varied from 0.4 cc. to 5.6 cc. It becomes necessary, therefore, to determine this factor for each soil and to make a correction accordingly.

The second error consists in assuming that the absorption of barium hydroxide is immediate. This assumption was found to be incorrect. It was found that fixation of barium hydroxide by a soil was complete when the mixture was heated in a water bath for one hour at the temperature of boiling water.

The effect of this treatment is shown in the following table:

TABLE II—BARIUM HYDROXIDE ABSORBED EXPRESSED AS LIME (CAO). PARTS PER MILLION DRY SOIL

Lab. No.	Absorbed immediately	Absorbed during one hour standing in boiling water	Lab. No.	Absorbed immediately	Absorbed during one-hour standing in boiling water
2619	425	963	3749	313	694
2620	425	940	3752	515	1209
2623	403	1187	3754	268	985
2624	425	896	3755	224	761

The higher figures obtained by the longer contact of the barium hydroxide and soil might be ascribed to the removal of the base from solution by the carbon dioxide of the air, in which case the longer exposure would introduce an error. To test this point 50 cc. of the standard barium hydroxide solution and 50 cc. of water were placed in a 500 cc. Kjeldahl flask. The unstoppered flask was then placed in a water bath maintained at the boiling temperature and allowed to remain one hour. The flask was then removed, 150 cc. water and 5 grams solid ammonium chloride added, and the mixture distilled in the ordinary Kjeldahl apparatus with the following results:

	Ammonia expressed in equivalent of N/10 acid Cc.
50 cc. barium hydroxide + 5 grams ammonium chloride....	51.4
5 grams ammonium chloride.....	1.6
Formed by barium hydroxide.....	49.8

TABLE I—LIME REQUIREMENT CALCULATED AS CAO. PARTS PER MILLION DRY SOIL

Lab. No.	Veitch method	Albert method	Lab. No.	Veitch method	Albert method
2333	1500	930	2626	0	0
2619	1100	67	3749	900	0
2620	1100	24	3750	0	0
2621	700	0	3751	0	0
2622	0	0	3752	900	134
2623	1100	156	3753	1400	560
2624	1000	201	3754	1000	0
2625	900	0	3755	500	0

preferable to calcium hydroxide, since the latter seems to form with the soil certain easily decomposed compounds which effect decomposition of ammonium chloride.

¹ Paper presented at the 48th meeting of the A. C. S., Rochester, September 8-12, 1913.

² *J. Am. Chem. Soc.*, **24**, 1120.

³ *Z. angew. Chem.*, **1**, 533.

As direct titration of 50 cc. barium hydroxide un-

exposed required 50 cc. of the tenth-normal acid, it is evident that the one-hour exposure does not introduce an appreciable error.

In view of the foregoing results, the writers propose the following modification of the Albert method:

The air-dried soil is prepared according to the method of the Association of Official Agricultural Chemists.¹

Place 25 grams of the soil in a Jena Kjeldahl flask. Cover with 50 cc. boiled distilled water and add 50 cc. tenth-normal hydroxide solution. Digest in a briskly boiling water bath for one hour with occasional shaking. Remove from the water bath, add 150 cc. distilled water and 5 grams solid ammonium chloride. Connect the flask with a nitrogen distillation apparatus, and distil. Collect the distillate (150 cc.) in tenth-normal acid and titrate, using methyl orange as indicator. The strength of the barium hydroxide is determined by titrating directly 50 cc. of the solution, using methyl orange as indicator. The difference between the two titrations, therefore, represents the amount of barium hydroxide absorbed by the soil.

The soil has a slight decomposition effect on the ammonium chloride. It is necessary to correct for this in each case by distillation of 25 grams of soil with 5 grams ammonium chloride, omitting the barium hydroxide solution. The ordinary Kjeldahl apparatus may be used, but care must be taken that stoppers and connections are free from alkali, which may have been left from previous use in the ordinary Kjeldahl distillations.

This method has been compared with the Veitch method on several samples of different types of soil and the results are given in the following table:

TABLE III—LIME REQUIREMENT CALCULATED AS CAO. PARTS PER MILLION DRY SOIL

Lab. No.	Description of soil	Modified	
		Veitch	Albert
2619	Dunkirk clay loam.....	1100	963
2620	Dunkirk clay loam.....	1100	940
2621	Dunkirk clay loam.....	700	694
2623	Dunkirk clay loam.....	1100	1187
2624	Dunkirk clay loam.....	1000	896
2625	Dunkirk clay loam.....	900	694
3749	Dunkirk clay loam.....	900	694
3752	Dunkirk clay loam.....	900	1290
3754	Dunkirk clay loam.....	1000	985
3755	Dunkirk clay loam.....	500	761
15405	Volusia loam.....	1912	1836
15407	Volusia loam.....	1434	1321
15409	Volusia loam.....	1434	1749
15413	Volusia loam.....	1434	1344
15425	Volusia silt loam.....	1912	2531
15427	Volusia silt loam.....	2390	2620
15430	Volusia silt loam.....	1673	2307
15432	Volusia silt loam.....	2629	2352
15443	Dunkirk clay loam.....	1673	1768
15445	Dunkirk clay loam.....	717	1232
15449	Dunkirk clay loam.....	1195	1456
13151	Volusia silt loam.....	1195	1344

The results obtained by the new method agree very well with those obtained by the Veitch method, and since there is no apparent method of standardizing either, it may be assumed to be just as correct.

The new method possesses the great advantage of rapidity, and if the details are carefully observed, it is very easy to obtain concordant results.

N. Y. STATE COLLEGE OF AGRICULTURE
CORNELL UNIVERSITY, ITHACA

¹ U. S. Dept. of Agric., Bureau of Chemistry, *Bull.* 107, 14.

AN INTERESTING SOIL WATER QUESTION IN BRITISH GUIANA

By MAURICE BIRD¹

Received September 15, 1913

Some years ago, Harrison² first called attention to the markedly alkaline condition of the soil water underlying the sugar estates fringing the coast of British Guiana, and its pernicious effect upon the growth of the sugar cane; and since this interesting problem is one to be very appropriately recorded in the pages of *THIS JOURNAL*, the writer has prepared the following brief account of it.

The appended analyses are typical of the sugar soils of British Guiana, and indicate their wonderful fertility from a standpoint of plant food. The yield and quality, however, of the cane grown upon them is very often disappointing, and this is due to the fact that, many of these lands lying below sea level, deep and thorough drainage is well nigh impracticable, with the results that as the soil slowly and continuously decomposes, the surrounding and underlying water becomes charged with alkaline mineral matter, the product of this decomposition, and this alkaline material entering through the roots, acts in a very deleterious manner upon the juice of the cane.

	Soil from Pln. Albion, Berbice (Coastal estate)	Soil from Pln. Friends, Berbice (River estate)	Soil from Pln. Hampton Court, Essequibo (Coastal estate)
Water and volatile matter.....	18.050	19.660	14.503
Insoluble matter.....	66.250	65.609	66.915
Iron and aluminum oxides.....	13.780	14.503	17.496
Lime.....	0.345	0.134	0.316
Magnesia.....	0.629	0.431	0.504
Potash.....	0.458	0.495	0.501
Soda.....	0.148	0.110	0.112
Phosphoric acid.....	0.248	0.256	0.224
Nitrogen.....	0.172	0.351	0.196

NOTE—Though weighed as ferric oxide some of the iron in these soils is in the ferrous form.

The excess of magnesia over lime in the above is very noticeable, and this appears to be the case throughout in the alluvial soils of the colony.

Coming now to the soil waters, the writer examined a great many under varying conditions of rainfall etc., finding the alkali, as determined by titrating with decinormal sulfuric acid, to range from a trace to 480 parts per million of water, when calculated as sodium carbonate; while the total mineral matter, determined by evaporation of the water rose to over one per cent of the water. This saline material entering the roots of the growing cane was found to produce from three to five times the quantity of ash in the juice that is found in the juice of cane grown on well drained soils. This ash, or mineral matter, of the juice concentrating in the molasses from the process of the sugar factory was found (as so lucidly described by Geerligs)³ to form uncrystallizable compounds with the sucrose, whereby much sugar is lost. In order to break up these compounds and render the sugar available it becomes necessary to employ some

¹ Chemist to the New Colonial Co., Ltd.

² *West Indian Bulletin*, 9, I, 1-39.

³ "Cane Sugar and its Manufacture," by H. C. Prinsen Geerligs.

such method, as osmosis or the Steffen process, as is in use in the beet sugar industry.

Since the soil water contains a large proportion of magnesia, which in the cane juice exercises an especially deleterious effect in restraining the crystallization of sugar, the experiment suggested itself to the writer of precipitating the magnesia from the soil water with a solution of hydrate of lime. As this proved highly successful, large quantities of lime (from two to three tons per acre) were applied to a large tract of sugar lands, with the result that the juice of the subsequently grown cane was very markedly improved.

SUMMARY

One of the chief obstacles to profitable sugar production in British Guiana is the highly saline character of the soil water, to overcome which every effort should be made to achieve deep and thorough drainage, which can be most advantageously supplemented by heavy applications of slaked lime to the land. Where these remedies are not practised a large loss of sugar in the factory can be obviated only by employing a special process, such as either of those indicated above, to separate the sugar from the abnormal quantity of mineral matter present.

PLN. ALBION, BERBICE
BRITISH GUIANA

MICROORGANISMS IN COMMERCIAL LIME-SULFUR¹

By C. A. PETERS AND A. W. BROOKS

Received October 13, 1913

Manufacturers of commercial lime-sulfur have been troubled for some time by the occasional thickening of their product when stored in barrels. As far as can be ascertained second-hand, wooden barrels of about 50 gallons' capacity are used in handling the product, and of a large number of barrels filled at the same time with the same material only an occasional one will develop the thickened material.

The nature of the thickened product has not been understood. In consistency it resembles a thin ketchup. In color it is nearly white, although seeming to be tinted red by the lime-sulfur mother liquor. The solid matter of the mixture remains in suspension settling but slightly if at all.

A qualitative examination, made by the writers, of a sample of this thickened material revealed a number of things which may be listed as follows: (1) When such lime-sulfur ketchup was filtered and dried the residue was largely sulfur soluble in carbon disulfid. (2) No sulfids, sulfites, or thiosulfates were present in the washed residue. (3) When thickened lime-sulfur containing the suspended material was heated, a clear solution was obtained which was evidently the original concentrated lime-sulfur solution. These results indicated that the precipitate was largely, if not entirely, sulfur. This idea was confirmed by the approximate quantitative conversion of the residue from portions of the thickened lime-sulfur mixture into barium sulfate. Such residues filtered on asbestos or paper were washed with water

until the filtrate was colorless and either dried about 15 hours in an electrically heated oven at 65-70°, and weighed, or converted into barium sulfate and weighed. The results are given in Table I.

TABLE I. CONVERSION OF RESIDUAL SULFUR INTO BaSO₄

No.	Weight of residue on asbestos	Sulfur calculated from BaSO ₄	Difference Gram
	Gram	Gram	
1	0.0365	0.0384	+0.0019
2	0.0431	0.0474	+0.0033

The amount of sulfur registered in Experiment 1, 0.0365 gram, was transferred to a beaker with the asbestos on which it was filtered. The whole mass was boiled 15 minutes with 50 cc. of a 10 per cent solution of caustic potash, and the sulfur oxidized by 50 cc. of ordinary 3 per cent solution of hydrogen peroxide. The mixture was then made acidic with hydrochloric acid, filtered through paper and washed, a solution of barium chloride added to the filtrate, and the precipitate of barium sulfate dried, heated, and weighed.

In Experiment 2, a 5 cc. portion of the thickened lime-sulfur mixture was filtered on asbestos, the residue was washed until the filtrate was colorless, dried about 15 hours at 65-70° and weighed. A duplicate portion was filtered on hardened paper, the washed residue separated from the paper was treated in a beaker with caustic potash, and precipitated and weighed as barium sulfate, as just described. The figures as given are multiplied by two before insertion in the table so that they may be compared directly with those of Experiment 1. The results are vitiated by the occlusion of potassium salts by the barium sulfate, and in Experiment 1, in addition, probably, by the silica from the asbestos, but they show an approximately quantitative conversion of the sulfur into barium sulfate.

It seeming to be established that the precipitate in the lime-sulfur ketchup was due to a mass of suspended sulfur, ineffective attempts were made to reproduce this characteristic ketchup substance by heating various lime-sulfur solutions until precipitation took place. None of the concentrated mixtures resulting resembled at all the original ketchup substance and microscopical examination of the residues showed masses of crystals which could have been only sulfur.

When, however, the original ketchup mixture was examined under the microscope the first real light was shed on the problem. The material consisted of masses of long threads, and motil rods were in abundance. The threads separated from the lime-sulfur liquid by filtering and washing, and, viewed in a water medium magnified 480 x, developed in a few minutes cross striations, and in the course of an hour or so some of the threads divided at the cross lines. In a few hours, after further changes, in place of the threads only spherical cells remained, the position of some of the threads being definitely marked on the microscope slide by a row of these spherical bodies. This description indicates that the solid matter in this lime-sulfur ketchup is due to microorganisms of a group closely allied to *Beggiatoa*.

¹ Material and funds for this work were furnished by the Bowker Insecticide Company of Boston, Mass.

This identification was confirmed by Dr. van Suchtelen of the Department of Microbiology.

The source of the infection by the microorganism is not known but the facts outlined in the first paragraph that only one barrel out of a possible hundred develops the organism and that the barrels used are necessarily second-hand, point to the previously inoculated barrel as the source of the trouble.

As it appears unusual that these microorganisms should appear in quantities in lime-sulfur concentrates data regarding the mixture may be of interest.

Density.—The densities of the ketchup mixture, the filtrate from it and of other lime-sulfur solutions were taken in an ordinary specific gravity bottle of 25 cc. capacity, with an open capillary tube, at room temperature which was 25°. The results are recorded in the following table:

TABLE II

No.	MATERIAL	Observed density	B. ° from commercial scale	REMARKS
1	Water	0.9966	Check
2	Lime-sulfur ketchup	1.3047	34.0	
3	Lime-sulfur solution	1.2996	33.6	Filtrate from Expt. 2
4	Lime-sulfur solution	1.3020	33.7	Ketchup heated until solution resulted and loss of volume made up
5	Lime-sulfur solution	1.2992	33.6	Duplicate of No. 4
6	Lime-sulfur solution	1.3214	35.3	Ketchup heated until solution resulted and loss of volume not made up
7	Lime-sulfur solution	1.3078	34.2	Same as No. 6 except heated with air condenser
8	Lime-sulfur solution	1.3072	34.2	Same as No. 6 except heated under return water condenser

An examination of the data in Experiments 7 and 8 shows that the original lime-sulfur solution in which the microorganisms developed was of the maximum density, 1.3075 (34° B.), for commercial preparations, and Experiment 3, that the filtrate from the ketchup was of a density of 1.2996 (33.6° B.), which is still slightly stronger than necessary for the trade. It is further seen, Experiments 2, 7 and 8, that the density of the clear liquid is only slightly altered (—0.008) by the withdrawal of sulfur by the microorganisms. Experiment 6 as compared with 7 and 8 shows how the density of these concentrated solutions is changed (+0.015) by the withdrawal of a small amount of water—less than $\frac{1}{25}$ — $\frac{1}{50}$ of the total volume in this case.

Sulfur in Suspension.—The amount of sulfur per cubic centimeter in suspension in the bodies of the microorganisms in the ketchup is 0.0043 gram as obtained from Experiment 2 in Table I.

SUMMARY

Microorganisms of *Beggiatoa*, or a closely related group, have been found to be the cause of an apparent precipitate of sulfur occurring in commercial lime-sulfur concentrates, making the whole mass of the consistency of thin ketchup. Some data regarding this thickened lime-sulfur is given.

The further study of the microorganisms, their iden-

tification, the sources of infection, and means of prevention are being investigated.

DEPARTMENT OF GENERAL AND AGRICULTURAL CHEMISTRY
MASSACHUSETTS AGRICULTURAL COLLEGE, AMHERST

THE ASSAY OF INDIVIDUAL PLANTS OF DATURA STRAMONIUM L., DATURA TATULA L. AND OTHER SPECIES AND VARIETIES¹

By F. A. MILLER AND J. W. MEADER

It has been stated in a recent communication² that the examination of individual plants of the *Daturas* for their total alkaloidal content has been undertaken as a means of following the effects of prolonged cultivation upon the percentage of alkaloids, and as a means of selecting high-yielding individual plants for breeding purposes. The present discussion is a continuation of this investigation, together with additional data upon other species and varieties not heretofore included. A review of the literature on stramonium was given in the original communication. This was followed by the assays of several individual plants of *Datura stramonium* L. and *Datura tatula* L. Seeds were collected from all the assayed plants and those from the individuals containing the highest and lowest percentages of alkaloids from each of the two species were planted May 30, 1912. The results obtained from these plantings are considered in the present discussion.

The conditions of growth were practically the same as those under which the parent plants were produced. The soil, a stiff clay loam though not identical, was that of an adjacent field and of a similar physical character. The plot was fairly uniform except for an excess of sand and gravel at one end. The plants growing at this point were smaller and less vigorous than the others. When about three inches high they were thinned to four feet in the row. Cultivation was begun at this time and continued throughout the growing season.

Eight plantings were made, four of *Datura stramonium* L. and four of *Datura tatula* L. These were made from the highest and lowest yielding individuals from each of the two species, as given in the original communication. The plants indicating these extremes assayed 0.55 per cent and 0.46 per cent in *Datura stramonium* L. and 0.65 per cent and 0.47 per cent in *Datura tatula* L. Four of the above plots received an application of normal commercial fertilizer at the rate of six hundred pounds per acre. This was applied when the plants were about one foot high.

The collection of samples of leaves for assay from individual plants of each of the eight plots was made early in September. These samples were dried at room temperature, granulated and sealed in amber bottles until assayed. Following are the results obtained from nineteen selections of individual plants from *Datura stramonium* L. Ten of these were from the high- and nine from the low-yielding parent.

¹ Paper presented at the 47th meeting of the A. C. S., Milwaukee, March, 1913.

² 8th Int. Cong. App. Chemistry, 17, 57.

TABLE I—*Datura stramonium* L.

Highest plant originally assayed 0.55 per cent

Without fertilizer			With fertilizer		
No.	Source	Assay Per cent	No.	Source	Assay Per cent
B-980	Parent plant	0.55	B-980	Parent plant	0.55
B-1349	Selection	0.50	B-1360	Selection	0.67
B-1351	Selection	0.56	B-1361	Selection	0.66
B-1352	Selection	0.50	B-1362	Selection	0.62
B-1353	Selection	0.54	B-1363	Selection	0.65
B-1354	Selection	0.42	B-1364	Selection	0.48
Average, 0.50			Average, 0.61		

Lowest plant originally assayed 0.46 per cent

Without fertilizer			With fertilizer		
No.	Source	Assay Per cent	No.	Source	Assay Per cent
B-982	Parent plant	0.46	B-982	Parent plant	0.46
B-1355	Selection	0.58	B-1357	Selection	0.64
B-1356	Selection	0.57	B-1368	Selection	0.68
B-1365	Selection	0.58	B-1369	Selection	0.58
B-1366	Selection	0.65	B-1370	Selection	0.71
B-1367	Selection	0.63	Average, 0.64		
Average, 0.60					

The *Datura tatula* L. selections, of which there were ten each from the high- and low-yielding parents, gave the following results:

TABLE II—*Datura tatula* L.

Highest plant originally assayed 0.65 per cent

Without fertilizer			With fertilizer		
No.	Source	Assay Per cent	No.	Source	Assay Per cent
B-984	Parent plant	0.65	B-984	Parent plant	0.65
B-1344	Selection	0.53	B-1378	Selection	0.72
B-1348	Selection	0.56	B-1379	Selection	0.75
B-1376	Selection	0.77	B-1380	Selection	0.69
B-1377	Selection	0.59	B-1381	Selection	0.73
B-1383	Selection	0.64	B-1382	Selection	0.44
Average 0.62			Average, 0.68		

Lowest plant originally assayed 0.47 per cent

Without fertilizer			With fertilizer		
No.	Source	Assay Per cent	No.	Source	Assay Per cent
B-985	Parent plant	0.47	B-985	Parent plant	0.47
B-1341	Selection	0.47	B-1371	Selection	0.66
B-1342	Selection	0.45	B-1372	Selection	0.50
B-1343	Selection	0.52	B-1373	Selection	0.48
B-1346	Selection	0.45	B-1374	Selection	0.53
B-1347	Selection	0.57	B-1375	Selection	0.54
Average, 0.49			Average, 0.54		

A small plot of *Datura ferox* L. was grown from seed obtained from Haag & Schmidt, of Erfurt, Germany. Four selections were made and samples of leaves from these selected plants assayed as follows:]

TABLE III

No.	Source	Assay Per cent
B-1345	<i>Datura ferox</i>	0.53
B-1350	<i>Datura ferox</i>	0.62
B-1358	<i>Datura ferox</i>	0.70
B-1359	<i>Datura ferox</i>	0.66

A small planting of *Datura humulus flava* was made of seed from the above source. A mixed sample of leaves assayed 0.42 per cent. Individual selections

could not be made on account of the failure of the plants to produce seed. This was due to the late planting and injury from early frost. The plants did not flower until September and were extremely sensitive to frost.

The foregoing figures indicate a considerable range of variations in the percentage of alkaloids as found in the individual plants. This variation in the progeny of both the *Datura stramonium* L. and *Datura tatula* L. selections is greater than that of the two parent plants. In the species *stramonium* this is 0.09 per cent in the parents, while in the progeny it is 0.23 per cent for the selections from both the fertilized and non-fertilized plots. The highest yielding plant was produced by the low parent upon a fertilized plot while the lowest yielding plant was produced by the high parent upon a non-fertilized plot. Contrary to expectations the higher averages were obtained upon the fertilized and non-fertilized plots from the low-yielding parent. For the fertilized plots these averages are 0.64 per cent from the low parent and 0.61 per cent from the high parent. For the non-fertilized plots they are 0.60 per cent from the low parent and 0.50 per cent from the high parent.

In the species *tatula* the variation of the two parent plants is 0.18 per cent while in the progeny it is 0.31 per cent and 0.32 per cent upon the fertilized and non-fertilized plots, respectively. The highest yielding plant was produced by the high parent upon a non-fertilized plot, while the lowest yielding plant was also produced by the high-yielding parent but upon a fertilized plot. The latter was an abnormal plant producing few leaves and for this reason might be expected to give a low yield. The next lowest appears, according to expectation, in the progeny of the low parent and upon a non-fertilized plot. The averages in this case are the reverse of what was noted for the species *stramonium* and are according to expectations. The higher averages are obtained from the progeny of the high parent and from the fertilized plots. For the fertilized plots these averages are 0.68 per cent from the high parent and 0.54 per cent from the low parent. For the non-fertilized plots they are 0.62 per cent from the high parent and 0.49 per cent from the low parent.

Table IV shows extremes as noted in the parents and offsprings and the variations as found upon fertilized and non-fertilized soils.

The greater range of variations in individual plant yield as found in these second generation plants is probably due to the fact that the parent plants represented mixed strains. Such mixed strains resulting from promiscuous pollination might produce plants giving altogether different yields from the parents. When the original selections were made no precautions were taken to prevent cross pollination. This precaution is necessary with the *daturas* if known parentage is desired. It has not been conclusively shown that the property of a plant to produce a definite percentage of alkaloids is uniformly transmitted to the offsprings. Inbreeding or close pollination of all selected plants is necessary in the study of the transmission of such

a character. The results so far obtained indicate that the seeds from open pollinated plants are either of composite parentage or that the character under consideration is not uniformly inherited. The results

TABLE IV
Datura stramonium

	Assay— Highest yielding plant	Assay— Lowest yielding plant	Variations Per cent
	Per cent	Per cent	
Parent plant	0.55	0.46	0.09
Non-fertilized.....	0.65	0.42	0.23
Fertilized.....	0.71	0.48	0.23
<i>Datura tatula</i>			
Parent plant.....	0.65	0.47	0.18
Non-fertilized.....	0.77	0.45	0.32
Fertilized.....	0.75	0.44	0.31

seem to point toward the former supposition with certain exceptions. Some degree of uniformity is to be noted in the assays of these second generation plants. There is more uniformity among the individuals within the groups assayed than there is between these individuals and the parent plants. Considering only the non-fertilized plots in this respect the progeny of the high-yielding stramonium is most uniform. The parent assayed 0.55 per cent and the progeny 0.50 per cent, 0.56 per cent, 0.54 per cent and 0.42 per cent. This uniformity within the groups is greatest in the tatula selections and is sufficient to maintain the averages in the order expected. Taking the average assay of the progeny of the low-yielding parent from the non-fertilized plot as a unit, the averages from the other plots of this species follow in their expected order, *i. e.*, 1.00 : 1.10 : 1.26 : 1.38. In the species stramonium, however, the uniformity within the groups is not sufficient to maintain this order. In this case the order is 1.00 : 1.06 : 0.82 : 1.01.

Greater extremes in the alkaloidal yield of the individual plants have been located than were found in the original investigations. This is doubtless due to the small number of plants originally assayed. It is believed that such extremes can be determined immediately by the examination of a sufficiently large number of individual plants produced under uniform conditions. Whether or not the greatest extremes in the two forms under discussion have been reached can be determined only by further study. The location of the highest extremes is the principal object. The possibility of the fixation of this high-yielding property must then be determined by inbreeding. If such a procedure is possible, high-yielding strains or races of the alkaloidal producing plants can be developed for commercial purposes. With four exceptions all of the forty-three assayed plants have been inbred and mature seeds obtained from them for planting. Twenty crosses (hybridizations) have also been made between various individuals of the three species studied. A few reciprocal crosses have been made. The alkaloidal yield of these hybrid forms will be studied in comparison with the yield of the inbred parents and their progeny. Perfect uniformity in the behavior of any character cannot be expected in the first generation from inbred plants. This is due

to latent tendencies, the elimination of which may require two or more generations by inbreeding.

It has already been stated that another object of this investigation was to follow the effects of prolonged cultivation upon the yield of alkaloids. The idea that cultivation causes a decrease in the value of medicinal plants has been current for many years, but apparently without foundation. The results obtained are contrary to this belief and are an indication of what may be accomplished through cultivation and improvement. All plants in the experimental plots have been under cultivation two years. The original source of the seed from which the cultivated strains were started is known absolutely in the case of *Datura tatula* L., as wild plants a few inches high were transplanted from a vacant lot in Indianapolis to the experimental plot. Thus two years under cultivation is known to be correct for this species. This is not true, however, with *Datura stramonium* L. The seeds from which the original planting was made were obtained in the London market and may or may not have been gathered from wild plants. Mixed samples were collected for comparison from wild plants found growing adjacent to the experimental plots. Following is a table of the average assays of the wild and cultivated plants:

TABLE V—AVERAGE ASSAYS (PERCENTAGES)

<i>Datura stramonium</i>			
Source	1910	1912	1912
Original plants.....	0.50	Fertilized	Non-fertilized
High-yielding plant.....		0.61	0.50
Low-yielding plant.....		0.64	0.60
Wild plants.....			0.28
<i>Datura tatula</i>			
Original plants.....	0.58	Fertilized	Non-fertilized
High-yielding plant.....		0.68	0.62
Low-yielding plant.....		0.54	0.49
Wild plants.....			0.35

These averages indicate the beneficial effect of cultivation both with and without fertilizer. In most cases these averages are higher in the second year than in the first. The general averages of all the selected plants assayed this year is greater in each case than the averages of the plants originally assayed. The exceptions are most marked in the averages of the progeny from the low-yielding parent. In *Datura stramonium* the averages are equal to or greater than the original average.

These forms will be continued under cultivation. Seed from the highest yielding individuals will again be planted and the resulting plants assayed in the same manner as those previously examined. In addition to the original objects of the investigation, *i. e.*, the effects of cultivation and selection upon yield of alkaloids, the influence of hybridization upon this yield will also be noted. Other species and varieties will be included as seed supplies become available.

LABORATORY AND PLANT

DETERMINATION OF NITROGEN BY THE NITROMETER

By C. M. JOYCE AND HARRY LA TOURETTE

Received October 20, 1913

The nitrometer consists of a gas generating bulb fitted at the top with a two-way cock leading to a dissolving cup and a gas exit tube, and which has at the bottom a connection for a rubber tube leading to a leveling tube, the whole being filled with mercury to a level just below the upper cock; a cylindrical glass measuring tube graduated from 0-100 cc. connected to a leveling tube through a T tube leading to an equilibrium tube. The latter is shaped like an inverted 100 cc. pipette graduated downward below the bulb from 100-130 cc. The whole system is filled with mercury so that the measuring tube may be completely discharged by raising the leveling tube.

ADJUSTING THE EQUILIBRIUM TUBE

The volume of 100 cc. of dry air at 0° C. and 760 mm. under the temperature and barometric conditions

the leveling tube so that the level is the same in the three tubes. The volume of gas in the equilibrium tube is then read and compared with the calculated volume at the time, a correction in the subsequent gas readings in the measuring tube being made accordingly.

NITROGEN IN POTASSIUM NITRATE

Approximately 0.4 gram potassium nitrate is placed in a weighing tube, dried two hours at 110° C., desiccated 24 hours over sulfuric acid and weighed exactly by difference into the cup of the gas generating bulb. This is dissolved in 9 cc. 95 per cent sulfuric acid added through a siphon thistle tube, entering the top of the dissolving cup through a tight-fitting rubber stopper. When the salt is dissolved it is drawn into the gas generating bulb and followed by two washings 1.5 cc. each of 95 per cent acid. The bulb is then shaken with a motion normal to its long dimension until the volume of gas determined by a rough paper scale pasted on the leveling tube becomes constant, this operation taking from 3 to 5 minutes.

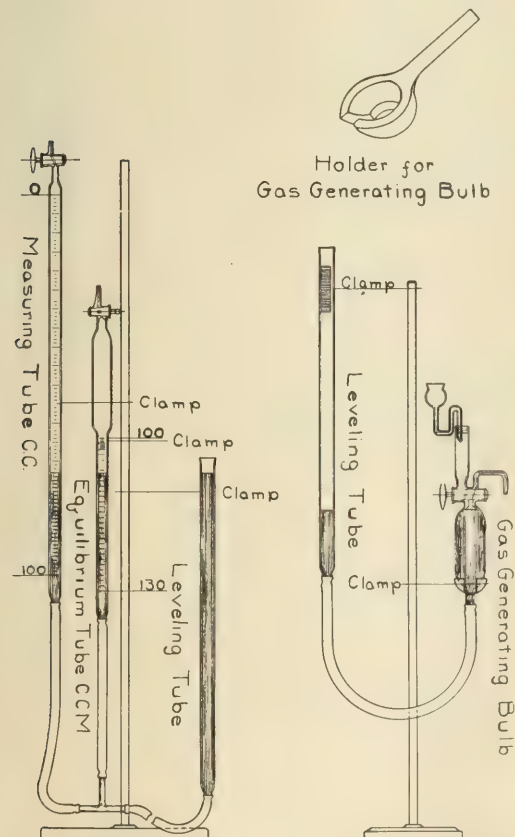
The gas is passed into the measuring tube and after standing 5 minutes the leveling and measuring tubes are so adjusted that the level in the equilibrium tube reads 100 cc. and is the same as the level in the measuring tube. The reading of the latter is then taken. As the temperature and barometric conditions, in so far as they affect the measured volume of the gas, are automatically compensated by the equilibrium tube, and as the gas is washed with sulfuric acid and is, therefore, dry, the percentage of nitrogen may be calculated directly, correcting only for the calibration of the equilibrium and measuring tubes. Seventeen determinations made when the room temperature ranged from 20-28° gave 13.71 per cent nitrogen, the theoretical being 13.84 per cent.

EFFECT OF ROOM TEMPERATURE

It was noted that the nitrogen determinations of pyroxylin when the room temperature was over 30° C. appeared abnormally high. Determinations of potassium nitrate were accordingly made at temperatures of 31-35° when the theoretical percentage was obtained. This would indicate that the solubility of nitric oxide in 95 per cent sulfuric acid diminishes practically to zero under these conditions. Nitrogen determinations of a well pulped sample of nitrocellulose were made at room temperatures ranging from 25° to 35° C. with the result that the apparent percentage increased beginning at 27° C., being 0.03 higher at 28°, 0.07 at 29°, 0.10 at 29.5°, 0.13 at 30°, 0.20 at 30.5°, and 0.23 from 31.0° to 35.0°.

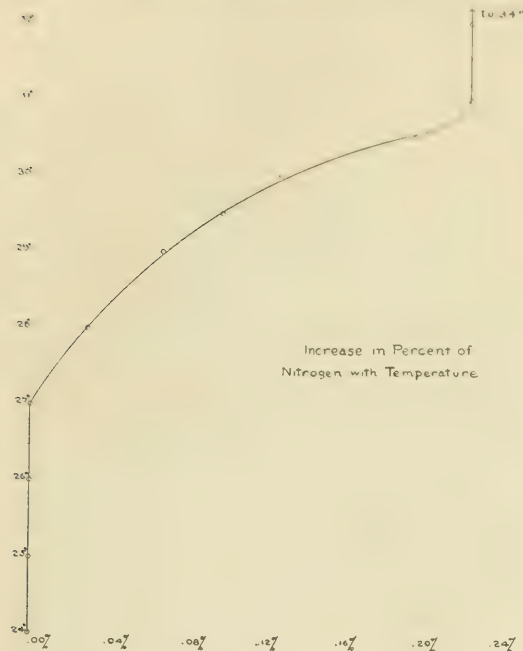
The results on nitrocellulose had been previously corrected for solubility of nitric oxide in sulfuric acid, the correction being based on the difference between the found and calculated values for potassium nitrate. This correction amounted to approximately 0.10 per cent and would account for about half the difference observed when nitrocellulose was determined at the temperatures before cited.

The greater apparent increase in nitrogen in pyroxylin over potassium nitrate with rise of temperature can be accounted for only by the partial breaking up of the cellulose into carbon monoxide and carbon dioxide.



prevailing at the time is calculated, three drops of 98 per cent sulfuric acid are drawn into the tube and the level of the mercury fixed in accordance with the calculation. The cock of the tube is then closed and sealed with melted paraffin. The volume in this tube may be confirmed at any time by opening the measuring tube and adjusting

The formation of carbon dioxide has been partially investigated, the contents of the measuring tube from determinations made when the temperature was over 30° C., having been passed through an absorption tube filled with barium hydrate solution. This method



offers some difficulties, owing to the small quantity of carbon dioxide, the presence of which has been determined only qualitatively thus far. The exact measurement of this gas and the formation of carbon monoxide will be investigated later.

Duplicate Kjeldahl determinations of the sample of nitrocellulose determined at varying temperatures were 0.09 per cent below the figure obtained with the nitrometer between 20° and 28° . This difference is within the limit of error of the two methods.

LIMITATIONS OF NITROMETER

The nitrometer gives results reliable within 0.02 per cent on nitrate nitrogen, using 0.4 to 0.5 gram sample. It is not available for the determination of nitrogen in celluloid or other substances containing carbon ring compounds which appear to prevent the complete liberation of nitric oxide in the presence of sulfuric acid and mercury.

SUMMARY

Besides the corrections for calibration and standardization of the nitrometer in accordance with temperature and barometer, the gas readings should be corrected for solubility of nitric oxide, which diminishes when the temperature goes above 28° C., and the formation of other gases by the breaking up of the cellulose molecule which increases.

The following table gives the algebraic sum of these two corrections for temperatures ranging from 20° to 35° C.:

Temp.	Cc.	Temp.	Cc.
20.0-27.5	+0.90	30.0	-0.14
28.0	+0.74	30.5	-0.70
29.0	+0.34	31.0-35.0	-0.94
29.5	+0.10		

ARLINGTON CO., ARLINGTON, N. J.

LABORATORY COLUMN STILL

By H. K. BENSON

Received September 22, 1913

In the description¹ of the equipment of the chemical engineering laboratory of the University of Washington, Fig. 9 of Plate 1 shows the location of an alcohol still. During the last year, through the kindness of a local manufacturer, a working model of a continuous column still has been installed, which has given excellent results in operation.

The still, which is made of copper, consists essentially of a preheater, primary column and rectifying column. The general plan of construction is shown in the sectional drawing, Fig. 1, and photo of the installation,

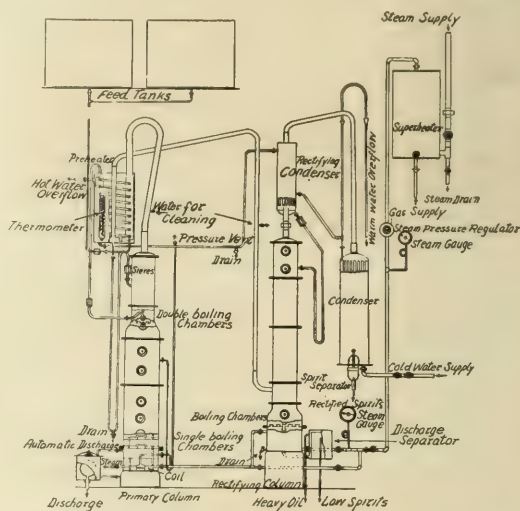


FIG. 1

Fig. 2. It has a total cubic content of 9.24 gallons, water measure, and is capable of producing from 2 to 4 proof gallons of alcohol in 8 hours.

The liquid to be distilled is fed by gravity into the preheater from small storage tanks. The heat is furnished in part by the vapors from the primary column and in part by radiation from water which has become hot in the rectifying condenser.

Thus the hot liquid enters the primary column and is discharged on to the double boiling chambers where the volatile portions are vaporized while the residues pass downward through a trap, or automatic discharge. The vapors next pass into an enclosed annular ring in the preheater, the heavier portions condense while the lighter pass over into the rectifying chamber, are subjected to repeated condensation and vaporization and finally constitute the high proof alcohol.

Steam is drawn from the heating system, passes through a superheater and thence into a pressure

¹ THIS JOURNAL, 4, 609 (1912).

regulator. For experimental work dealing with the production of ethyl alcohol from sulfite waste liquor

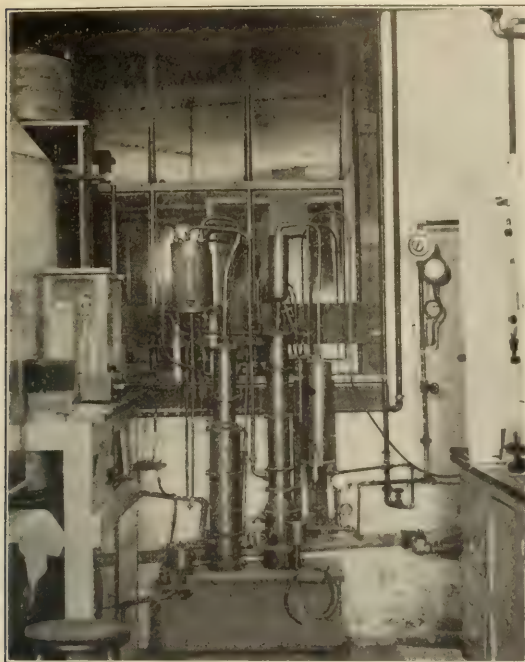


FIG. 2

and of methyl alcohol mixtures suitable for denaturing purposes, a steam pressure of less than 5 pounds was found efficient.

LABORATORY OF INDUSTRIAL CHEMISTRY
UNIVERSITY OF WASHINGTON, SEATTLE

AN IMPROVED LABORATORY BURNER

By CHAS. P. FOX

Received September 16, 1913

In laboratories where air currents are troublesome, a cylindrical wind shield, independent of the burner, is often employed. For use with any of the common types of laboratory burners, the attachment shown in the accompanying photograph is much more convenient.

It consists of an inverted sheet metal cone 5 inches long, 2 inches in diameter at bottom, and 3 inches at top, and supported by a 3-armed frame attached to the burner tube.

By making the support sufficiently rigid the triangle holding the crucible in ash determinations and the gauze when heating small beakers may be placed directly across the top of the shield.



Any tinsmith can fashion and attach the shield, using for the 3-armed frame an ordinary chimney support (E. & A., No. 2613 or Sargent, No. 1080).

This type of burner, as improved, has been found very useful in light laboratory work. The improvement has been in use several years and, as far as known, is original.

AKRON, OHIO

ADDRESSES

BIOCHEMISTRY¹

By CARL L. ALSBERG

I did not come to Rochester with the intention of making a speech, but find—I am sorry to say—that Prof. Chambers expects me to talk. He made the request—or, shall I say, demand—as we came to this room. I find that I am driven to the usual refuge of those who have to speak when they would rather be silent—that is, I will take refuge in the history of my subject.

This subject has, I think, some general interest because originally no very definite distinction was made between biochemistry and any other kind of chemistry. One of the first real biochemists was Lavoisier, whom all matter, whether living or dead, interested. He performed the first calorimetric experiments. He was the inventor of the ice calorimeter, and showed that animal heat was the result of oxidation. All the chemists of that generation, and the immediately succeeding one did biochemical work. I need only cite Liebig, who is perhaps in some ways the greatest of all biochemists. Unfortunately, about the latter part of Liebig's life chemists lost interest in biochemistry. This was due very largely to the sudden and

tremendous development of organic chemistry, which was brought about by the discoveries of men like Hofmann and Kekulé. It was so easy to make new synthetic substances, and thereby gain a sort of immortality, even though the main result of putting a chlorine atom here and a bromine atom there was to fill up Beilstein. In consequence, thoroughly trained chemists did not busy themselves with subjects that were really important in the elucidation of that matter which is found in living organisms, and which forms the physiological basis of life. The scientists in biology and medicine needed such information. The chemists did not give it to them. Consequently, physicians and physiologists who were ill-equipped for chemical research were forced to carry forward the work of biochemistry. Though the net result of their work made decidedly for progress, only too often it created confusion and artificial difficulties. Even the best biochemists of those days make us wonder why they did not pursue their chemical investigations as far as the chemical methods of that day would permit. The answer is, I think in many cases, that they were not real chemists but physiologists with a chemical veneer. Fortunately, this has been changing during the past decade, largely owing to the work of Emil Fischer. While we recognize in him a master of chemical technique, we may be certain that in a measure, at any rate, the preëminent position which he occupies

¹ Chairman's address, Biological Chemistry Section, 48th meeting, A. C. S., Rochester, September 8-12, 1913.

among the chemists of his time is due to his clear conception of the really most important work in organic chemistry along biochemical lines. Fortunately, more and more organic chemists are following in his footsteps, and are devoting their attention to substances which occur in living things. I wish here to make a plea for more of this sort of work in America. I believe that the rewards and recognition for knowledge of chemistry applied in biochemistry are great, because the work of the biochemist will be applauded not merely by chemists, but also by zoologists, botanists and physicians. A biochemist has a wider audience because his work presents a more general appeal than the work of organic chemists upon such subjects as dyestuffs and the like. Further, I wish to point out the value of instruction in allied subjects. Not every organic chemist can successfully attack all biochemical problems. Besides his organic chemistry, other experience in physiology, and above all, experience in dealing with substances which do not crystallize is necessary. In many cases it is difficult to conduct biochemical research because the biochemist must very frequently begin with the smears, which the organic chemist consigns preferably to the slop jar. While the things which will not crystallize interest the organic chemist less, they are the very classes of substances with which the biochemist must deal. Great care, great patience and a knowledge of colloids are required of the organic chemist who wishes to work in biochemistry, but I feel confident that the reward for such men is great, not merely in pure science, but also in the industries and in the arts.

The history of biochemistry in America is similar to that abroad. In America it developed first in the seventies and eighties in the medical schools of the country; and, at that time, it was controlled by physicians and physiologists abroad. The subject was narrowed to the consideration of biochemistry as affecting the life of man; that is to say, the chemical side of physiological processes of the human body together with such considerations of bacteriological chemistry as affect man in health and in disease. This phase of biochemistry is cared for very adequately and acceptably by the American Society of Biological Chemists, the first biochemical society to be formed in America.

The phases of biochemistry which the American Chemical Society can very naturally expect to encourage are quite distinct from the aims of the American Society of Biological Chemists. Our usefulness will include the biochemistry affecting agriculture, phytochemistry in particular, and such industrial processes as are based upon biochemical reactions. For example, the more exact study of the chemical composition of fruits, grains, and food products. It must be admitted that, at present, we know only those chemical substances occurring in considerable amounts in such important grains as wheat and corn. The minor constituents in grains of much importance have not been identified with exactness. If we consider grains of less importance even this degree of knowledge can not be claimed.

Some of our most important modern industries, like those dealing with starch, artificial fabrics, leather tanning materials, glue and gelatin, meat packing and the flour milling industry require biochemists, and we are now training men to deal with such practical problems.

If our society confines itself to the activities already mentioned, there still remains a wide field of biochemistry uncared for, the biochemistry of the lower animals. This part of the biochemical work will become a part of the work in the zoological societies of the country. My view is that three societies of biological chemistry can well exist in America without competing in any way, each one caring for a specific need. These would include the biochemistry of the higher animals and its application to medicine; the biochemistry of the lower animals; and biochemistry in its application to plants, agriculture, and the industries.

BUREAU OF CHEMISTRY
WASHINGTON

THE PROGRAMS FOR THE SECTIONAL MEETINGS OF THE AMERICAN CHEMICAL SOCIETY A SUGGESTION¹

By BERNHARD C. HESSE

Suddenly confronted with the major responsibility for the programs for the nine meetings of the New York Section of the American Chemical Society for the current session, the question as to what results are to be aimed at took sharp and definite form in my mind.

The answer to that question, as nearly as it can be arrived at by observation of members of the audiences at these meetings and by interrogation of a number of them, can never be anything but a generalization or a number of generalizations, which appear to be about as follows:

1. We come to these meetings to hear a good, lively discussion and not to listen to a catalog of analytical results or numerical constants or detailed experiments. Final, conclusive and generalized results are what we are after.

2. Discussion, in order to be lively, should be prepared in advance and every one should have an opportunity to become acquainted with the general trend of the papers prior to the meeting.

3. Extemporaneous discussion too often leads very far afield and the real points of the paper read and in issue are not touched upon.

4. The meetings are too long and of too uncertain duration.

That these generalizations have a foundation in fact became evident by a number of walks through the various rooms of this building during meetings of this and of other societies. It is a safe estimate that, in general, there were quite as many men in the foyer, in the social room and in the restaurant as there were in the audience in Rumford Hall. Those on the outside frequently comprised a number of men who were eminently fitted to discuss the papers presented; on inquiry as to why they were not in Rumford Hall the general answer was to the effect that they were waiting for the conclusions to be stated and then they might have something to say; no sitting through the reading of the dry details for them! Following up some of these individuals, it turned out that although they were present when the final conclusions of the papers were stated yet they said nothing in the discussion and the explanation given was that while they did not agree with the conclusions stated yet they had not their material in such condition as to use it with convincing effect; generally they indulged in disparaging remarks of what little discussion had taken place; in not a few cases some have remarked that if they had only known the day before what so-and-so was going to say they'd have loaded for bear, and shot so-and-so's conclusions as full of holes as a sieve. Making due allowance for a little braggadocio they probably meant that under those circumstances they might have made a creditable opposition showing. The crucial question, however, is: "Would they?"

It is a fact that many of our members reside at a distance and it is imperative for them to leave the Chemists' Building before a definite time, say 10.30 P.M., in order that they may not be unduly delayed in their arrival home. Everybody knows that once a commuter's mind is on his train his mind is not on much else and particularly not on the subject matter of the paper; the fact is that he is anxious to have the matter over with so that he can have a moment's chat with some particular person in the audience and as likely as not, that particular person is not at that time in any particular hurry to leave and communication with him in the meeting-room is, to say the least, awkward and embarrassing, if not unfeasible. The unavoidable result needs no further portrayal here. We have probably each and all of us been through that experience.

¹ Chairman's address at the October 10th Meeting of the New York Section of the A. C. S., The Chemists' Club, New York.

This is not a complete statement of the problem nor of the facts but it probably contains the essentials and the salient points of both and will answer for a working basis for the consideration of a plan of action which may be capable of overcoming some of the defects just noted.

It is becoming more and more the practice at the large meetings of a number of technical and scientific societies to have the papers to be read at those meetings printed and distributed to the members in advance of the meetings. This plan tends to minimize these defects, at any rate. If now, the author were to be limited to a few moments to recapitulate in a few words the most important essentials and the debatable points in lieu of reading the entire paper and if one or more members could be induced to prepare a set and carefully worded discussion of such papers as lend themselves thereto also in advance of the meeting, the way seems to be open to complete overcoming of the foregoing defects if only the auditors will then do their part and critically think the subject matter over and properly fortify and equip themselves in advance of the meeting. If discussions under those circumstances be not lively and short and to the point as well as interesting and useful such failure must then lie in and be inherent to the subject matter, itself.

Of course, for sectional meetings the expense of printing the papers in advance is prohibitive; to base the program upon articles appearing in our own journals and of fairly recent date seems as though it should be feasible; at any rate, that is the suggestion I am now making, that sectional meetings could, with profit to all, be based, in part at any rate, upon one or more papers in recent numbers of our own journals and that one or more persons be invited to prepare a set discussion of such papers as lend themselves thereto, but in all cases such discussion is to be opened and closed in the briefest manner possible by the author or perhaps by some one the author might choose to designate. All who attend will have had opportunity to acquaint themselves in advance with the nature of the communication and its main points, conclusions and contentions.

Making this plan effective will put a greater share of responsibility on the audience and in view of the lethargy of the human being the all-important question is: "Will the audience do its share?"

For a time I was tempted to try this plan out during the present session, but having only recently had considerable and weighty proof of the enormous inertia of the human mind in the acceptance of a new order of things, I have refrained from such attempt and have contented myself with bringing my thought to your attention in this manner in the belief that if it corresponds in any degree to any real existing need that this Section can be depended upon to take such action in the premises as the merits seem to warrant.

90 WILLIAM STREET
NEW YORK CITY

EMPIRICAL REQUIREMENTS IN ASPHALT SPECIFICATIONS

By LEROY M. LAW

Received October 1, 1913

INTRODUCTION

The purchase of materials under specifications is a practice that is daily becoming more general. It is a natural outgrowth of the systematic study of one's requirements and the scientific development of products to meet them. The practice has reached its present broad application and usefulness largely through the aid of the chemist and it is in the interest of chemists engaged in bituminous work that this paper is primarily written.

Under ideal conditions, purchasing under specifications is beneficial to both consumer and producer. The former is enabled to state in precise terms his exact requirements in the way of material needs. This establishes quality and, as a result,

all competitors are placed upon an equal footing and competition resolves itself into the real objective, competition in price alone. To a producer, it means first of all that he is given an equal chance with others in the trade, and as all deliveries are to be rigidly inspected, he feels safe that another dealer cannot submit a profitless price in the hope of furnishing an inferior article.

The mutual understanding or, to use the definition of contract, the "meeting of minds," is brought about through the agency of the specification proper and it is, therefore, highly important that this feature should receive serious consideration. Its prime object is to define the requirements in terms which permit of ready interpretation, avoiding all possible uncertainties which may give rise to disputes under the contract. This point is vital and really forms the foundation of this great system, yet even in some of our most elaborate specifications its importance is frequently neglected. In many of the early types we have seen such requirements as "The material must be A. B. C. brand or equal thereto" and "the material shall have given satisfactory service under similar conditions for such a period of time." With such crude clauses specifications fail of their purpose for the actual requirements are at best but vaguely stated and the producer has no way of ascertaining if his wares are "equal to" or have "given satisfactory service" in the judgment of the person who reviews the bids and makes the award.

Such conditions especially unfair to the manufacturer are rapidly disappearing, yet to-day in many of the so-called scientific specifications, the adoption of requirements based on arbitrary methods of analysis has placed the honest producer in an equally uncertain and embarrassing position. It is to three such requirements which have gained and still hold surprising popularity in many current bituminous specifications that I now invite your attention.

DISCUSSION

The first stipulation of this character to be mentioned is that limiting the so-called "fixed carbon" and it is indeed difficult to understand just how this requirement even secured a foothold in asphalt specifications.

Fixed carbon is a test stolen from fuel chemistry, where it serves to indicate the coke remaining after the gaseous constituents have been removed by heating the material, with exclusion of air, under prescribed conditions. Those who have had any experience in fuel work whatever know full well that this test is purely empirical and that the variations among different operators, especially in different laboratories, is often considerable.

A committee of the American Chemical Society gave considerable study to the matter some years ago and in 1899 recommended the procedure¹ that is now followed in conducting this determination. It is to be understood however that this method is not applicable even to some fuels like the lignites which are very prone to spark. How much more inapplicable then will the method be to softer materials like the asphalts and road oils which have also the disagreeable tendency of foaming out of the crucible at certain stages of the heating?

Chemists should know that city illuminating gas, the source of heat, varies in different localities; in fact in some cities the composition is entirely different from that in others, hence a variation in heat, to say nothing of the difference in type and the condition of burners employed. It has also been found that the degree to which the platinum crucible is polished has also an effect on fixed carbon results and there are doubtless other sources of variation not as yet discovered.

The point is that asphalt chemists who advocate such requirements in their specifications, fail to realize these features

¹ J. Am. Chem. Soc., 21, 1116.

and their resulting effect on the limitations of accuracy. Fieldner, of the U. S. Bureau of Mines, in speaking of the fixed carbon test, makes the following statement in regard to coal and what he says in regard to coal is equally applicable to the fixed carbon in asphalts for the same procedure is used with both materials.

"The volatile matter and fixed carbon represent the relative proportions of gaseous and solid combustible matter that may be obtained from the coal by heating it in a closed vessel. This is done by heating a finely powdered sample in a small, covered platinum crucible, in the flame of a Bunsen burner or Méker burner for exactly seven minutes. The volatile matter consists mainly of the combustible gases: hydrogen, carbon monoxide, methane, and other hydrocarbons and some non-combustible gases such as carbon dioxide and water vapor. The volatile matter does not include water present in the coal as moisture at 105° C. (221° F.).

"The residue of coke left in the crucible after deducting the ash is reported as 'fixed carbon.' The 'fixed carbon' does not represent the total carbon in the coal, as a portion of this element is driven out in combination with hydrogen in the volatile matter; furthermore, 'fixed carbon' is not pure carbon, but still contains several tenths per cent each of carbon, hydrogen, and oxygen; from 0.4 to 1.0 per cent nitrogen; and about half the sulfur that was in the coal. It should be clearly understood that the terms 'volatile matter' or 'volatile combustible matter' and 'fixed carbon' do not represent any definite compounds which existed in the coal before heating. The method of determination is purely arbitrary and variations of temperature and rate of heating will cause variations amounting to several per cent; even with a strict adherence to the method recommended by the American Chemical Society, variations of three and four per cent in both the volatile matter and fixed carbon may occur in different laboratories. One of the most prominent factors in causing variations is the temperature at which the crucible is heated."

"It is especially pronounced in anthracite and semi-bituminous coal. It is not improbable for one laboratory to report 4 per cent and another 7 per cent volatile matter on the same sample of anthracite, or 14 per cent and 17 per cent, respectively on the same sample of Pocahontas coal. The different percentages of volatile matter were actually produced by different conditions of heat treatment. Caution must, therefore, be observed in making comparisons of the volatile matter and 'fixed carbon' in proximate analyses made in different laboratories. Even determinations made at the same laboratory by the same analyst may vary to the extent of 0.5 per cent."

If such wide variations do occur with coals what, then, should we expect when the method is applied to soft asphalts and even oils?

As a chemist of one of the large asphalt companies, I have observed this fixed carbon requirement enforced to extremes and yet to no purpose or benefit to the consumer. The yield of fixed carbon cannot be controlled in the process of manufac-

ture, unless through gross carelessness in coking material. In this case, the defects will be shown far more accurately by increased insoluble matter in the various reagents employed in bitumen analysis.

Inspection of the figures shows a variation in fixed carbon on the same samples of over 6 per cent in one case and nearly 9 per cent in the other. When experienced operators such as the above differ by these amounts on identical samples, is there any wonder that with chemists generally, the variations are even greater? It is to be regretted that chemists do not study the value of these tests before incorporating them in their specifications and extend to good materials and their honest manufacturers a just consideration. If fixed carbon in Baltimore is different from fixed carbon in Pittsburgh and, if in any one place the results are to vary from day to day, what possible value can the test have as indicating the value of a material? Furthermore, how is the manufacturer to test his products in every consumer's laboratory, to ascertain conditions prevailing in each of them?

Some days back it was our misfortune to have a shipment of asphalt rejected, because the fixed carbon as determined in the customer's laboratory ran from one-tenth to three-tenths in excess of the prescribed limit. I had previously tested the batch from which this shipment was made, and found the fixed carbon considerably below the requirements of the specifications. Think of a scientist holding up a material on such a narrow margin as this, when even the most precise chemical methods are seldom within this limit of accuracy, especially as carried out in ordinary commercial testing! An absurd feature of the case is that another carload from the same batch was accepted as meeting the requirements, the inspecting chemist doubtless being unconscious of the variation he was experiencing in his own laboratory.

But I leave the subject of fixed carbon to pass to another empirical requirement of still greater uncertainty, *i. e.*, the so-called paraffin determination.

This procedure is supposed to show the amount of hard or "scale" paraffin present in the material and is, therefore, considered to be an index as to its liability to crack in cold weather or granulate with age. The general procedure employed in this determination is doubtless familiar, consisting of distilling the material rapidly down to dry coke and collecting the distillate. The latter is then weighed, an aliquot portion removed, dissolved in alcohol-ether, chilled and the crystallized scale filtered off, dried and weighed. Many specifications prescribe that the scale shall not exceed a certain figure, yet few of them prescribe their modifications in detail. The results are that each customer performs the test in the manner most agreeable or convenient to himself, and the manufacturer has to stand for the whims and modifications introduced.

Usually the test is conducted in a glass retort, yet some operators substitute in its stead an iron one. That this may influence results matters little, so the manufacturing chemist must visit all these laboratories to become familiar with each chemist's details, return and endeavor to duplicate conditions.

Dow and Smith,¹ using an iron vessel, show the effects of different rates of heating, type of condenser, etc., and furthermore, express the belief that at certain heats soft paraffins may be converted into the scale form. In the face of these experiments and opinions we have chemists who insist that the higher the paraffin scale obtained the more accurate the method, their

RESULTS ON FIXED CARBON (PERCENTAGES)

Sample No.	213	215
Laboratory A.....	12.00	17.4
Laboratory B.....	13.62	16.85
Laboratory C.....	10.91	13.13
Laboratory D.....	12.52	17.54
Laboratory E.....	12.63	17.20
Laboratory F.....	17.10	22.00

ture, unless through gross carelessness in coking material. In this case, the defects will be shown far more accurately by increased insoluble matter in the various reagents employed in bitumen analysis.

Some weeks ago the writer prepared two samples of bitu-

¹ THIS JOURNAL, 5, 270.

¹ Engineering News, June 8, 1911.

claim being that "you can not get out more than there is in it."

In an effort to learn something as to the paraffin test as generally applied, the six laboratories who replied to the fixed carbon inquiry were also asked to determine paraffin scale in the same samples. They did so with the exception of one laboratory which for reasons not stated, declined to make the determinations. I trust that laboratory E realizes the unscientific status of the paraffin scale test and it was this realization that prompted them to decline to report on the subject.

RESULTS ON PARAFFIN SCALE (PERCENTAGES)

Sample No.	213	215
Laboratory A.....	3.6	2.8
Laboratory B.....	0.10 ¹	1.58
Laboratory C.....	2.7	1.49
Laboratory D.....	1.21	1.25
Laboratory E.....		
Laboratory F.....	4.13	3.04

¹ Material foamed considerably. Analyst is of opinion that there is no accurate method and results are only approximate.

The above results tend to make a laughing stock of the profession and are printed only with the hope that asphalt chemists may soon get together and study or eliminate these embarrassing subjects.

Our company is furnishing a certain material to one customer who limits paraffin to one per cent. From him we have had no complaint whatever, yet the same material is ineligible under another specification having been reported to contain paraffin in excess of four per cent. I ask you candidly which chemist is right, and what is the manufacturer to do under such conflicting evidence?

Turning now to a third requirement of questionable scientific value, and non-indicative of either quality or service results, I call attention to a requirement in many road oils and binder specifications which states that the material at, say, 50 penetration, shall have a specified minimum ductility. The idea is that the bitumen shall possess adhesiveness, a quality best shown by the ductility test and by concentrating to 50-penetration, the standard consistency for this ductility test, all materials are brought to a uniform basis of comparison.

Thus far, the idea is sound but the method of concentration, the all-important feature, is sadly and ignorantly neglected. Some chemists in a blind attempt at conserving ductility, stipulate that during concentration, the temperature shall not exceed, say 400° or 500° Fahrenheit. Others provide for "occasional" stirring, but generally they neglect the essential feature in asphalt treatment, namely the agitation. In hardening the softer asphalts, agitation plays if anything, a far more important role toward conserving ductility than does the mere restriction of temperatures. My interviews with inspecting chemists relative to this test, show that they are uniform only in following "no regular procedure."

Some of them use heat test residues which by accident have just reached 50 penetration or again this residue treated to a further heating on a hot plate or in an oven to obtain the desired consistency. Others concentrate the material from an oily state to asphaltic consistency in a single operation, either on a hot plate or in an oven, with or without agitation as suits their fancy and the manufacturer must ascertain and duplicate in his laboratory all of these eccentricities to find out the chance his material has of passing a so-called scientific specification.

On one occasion the writer submitted to a prospective customer a series of asphalt products varying in consistency from a maltha down to an asphalt cement. These were tested by the inspecting chemist who passed the harder materials, but rejected the softer ones, as absolutely lacking in ductility when reduced to 50 penetration.

The chemist allowed me to look over his results, and I observed that with the material requiring the least concentrations he had secured the highest ductility and in case of the fluid material requiring the greatest concentration to reduce it to 50 penetration, practically no ductility was obtained. All of the products were from the same primary material, the maltha, the harder ones being produced by refinery operation which neither he nor any one else could duplicate in the evaporation tins of the asphalt laboratory.

In the instance cited, the chemist's process was undoubtedly one destructive to ductility for the longer the heating required to reach 50 penetration the lower the ductility of the product. The individual in question avoided the issue by deciding that to his mind the test represented service conditions where no agitation of the material took place. And so I might go on with a number of other requirements without theoretical or practical significance, but why take up time or space?

Suffice it to say that such clauses as fixed carbon, paraffin scale, etc., in their present empirical state and coupled with a narrow and rigid interpretation are not only a discredit to the profession, but destroy the value of a sincere specification.

It has just been stated that the principle object of the specification is to lay before the manufacturer in a clear, concise manner the requirements that are to be met. When he is unable to interpret these with a reasonable and standard equipment, the purpose of the specification fails.

CONCLUSION

The rapid developments in bituminous highway work during recent years has been accompanied by an accumulation of inspection methods, desirable and questionable ones springing up together and the many young chemists in this field of work doubtless look upon them as methods of established, scientific value. Other chemists with only time for routine work of testing become advocates of such requirements as they might otherwise suppress. Furthermore specifications of one city or municipality are frequently copied from those of another which presuming from a longer experience in bituminous work is looked upon as a criterion in such matters.

And so by these and other unstudied procedures our asphalt specifications have been brought to this present empirical condition, and the time is at hand for chemists in this branch of the science to coöperate in weeding out the tangled field of laboratory methods.

No one chemist should, and no true scientist will, decide that check results in his own laboratory establish the reliability of a test or method of analysis. Such is at least to be expected. A true scientist will endeavor to ascertain what the procedure shows in the hands of others, presuming, of course, average qualifications in experience and skill.

If as a result of such study fixed carbon, paraffin, etc., are found to be of value, then it will be of interest to all concerned to adopt definite procedures and agree on the limitations of accuracy. If they cannot be developed into real scientific methods, capable of yielding concordant results in the hands of all qualified chemists, then they should, by mutual consent, be abandoned. In their present empirical condition they can not be of any possible assistance in determining the quality or even the uniformity of a product, but on the other hand, their employment frequently works injustice to valuable materials.

Until the status of these tests is better established would it be any more than fair to the manufacturer to omit such requirements from bituminous material specifications?

LABORATORY U. S. ASPHALT REFINING CO.
EAST BROOKLYN, BALTIMORE, MD.

CURRENT INDUSTRIAL NEWS

By W. A. HAMOR

SULFITE WASTE LIQUOR PROBLEMS

Paper for November 12, 1913 reports that in the manufacture of chemical woodpulp by the sulfite process, half of every cord so treated is dissolved by the liquor in which the wood is boiled, and is discharged into the adjacent rivers as waste liquor. According to the latest bulletin on pulpwood, issued by the Forestry Branch, Ottawa, the amount of pulpwood subjected to this chemical treatment in 1912 was almost 290,000 cords. Half of this amount was absolute waste. The average price of a cord of pulpwood is six dollars, so that this waste, reduced to its money equivalent, represents a loss to Canada of over \$800,000.

Nor is this the only loss, for by this process 140 pounds of sulfur are required to dissolve the waste materials out of each cord of wood. Some of the gases generated in the process are recovered, but most of the sulfur passes off in the waste liquor, and no method has yet been found to recover it for use a second time. Sulfur costs twenty-five dollars a ton, and the loss in this particular is equivalent to a money loss of over half a million dollars on the total amount wasted.

In view of the fact that each year more and more pulpwood is being manufactured into pulp by this process in Canada, the utilization of this waste liquor becomes an important problem. Even the most practicable method so far devised does not recover enough valuable products to make it pay.

The waste liquor contains many materials, such as oxalic acid, tannin extracts, dyestuffs and alcohol constituents which, if they could be easily recovered, would make the liquor of great commercial value; but in spite of the tremendous amount of work has been done on the subject, especially in Europe, the problem still remains for the most part unsolved. As the liquor also contains carbohydrates, it should be possible to obtain turpentine, and eventually it may be possible to obtain rubber from it. In furthering the solution of such problems and in eliminating other forms of wood waste, the new Forest Products Laboratories being established by the Dominion Government at McGill University will doubtless play an important part.

One use of the waste liquor mentioned above, that has been tried at Grand Mère, Quebec, where the Laurentide Company has large pulp and paper mills, consists in its utilization for street-watering. Experience has shown it to be as efficacious in keeping down dust as oil is, while the objectionable odor of oil is absent.

NICKEL A BY-PRODUCT IN THE UNITED STATES

The Geological Survey reports that there are no producing nickel mines in the United States. The output of nickel from domestic ores is merely a by-product from electrolytes of the copper refineries. Salts and metal equivalent to 328 short tons of metallic nickel were saved in domestic refineries in 1912 from both foreign and domestic ores. Nickel ore, "imported for consumption," is mostly from the Canadian deposits.

PRACTICAL CONSIDERATIONS AFFECTING CHOICE OF THERMOMETERS IN INDUSTRIAL PLANTS

In *The Institution of Mechanical Engineers*, Whipple points out that questions of first cost, up-keep, etc., must be considered in the selection of thermometers for either high or low temperatures.

As a rule the temperatures found throughout a steam plant may be taken with mercury thermometers, sockets, or mercury cups being placed in the steam pipes into which the mercury thermometers are placed. On the other hand, it is frequently troublesome to read the important thermometers in the plant,

and they often go unread. The thermometer at the foot of the smoke stack, and the one on each side of the economizer, although giving valuable information as to the efficiency of the plant, are frequently unnoticed. For this reason it is advisable to install resistance thermometers, which can be easily read on a galvanometer mounted in the boiler or engine house. When dealing with high superheater temperatures, a recorder or an alarm thermometer will be found of service.

Mercury thermometers are generally employed in cold storage work, but experience has shown that in the case of large stores—say ten rooms or over—it pays to install resistance thermometers. A great deal of time is spent in reading mercury thermometers throughout a large building which necessitates the opening and shutting of a number of doors, and which, in addition to the labor cost, is wasteful of power and tends to destroy the uniformity of temperature in the various rooms. The applications of pyrometers in works for the treatment of metals are very varied. One of the most important is the measurement of the temperature of the air in the hot air main of a blast furnace. If prime cost is not an overwhelming consideration, then resistance thermometers should be used connected to a Callendar recorder. Thermocouples may be used, but if an accuracy comparable to that of the resistance thermometers is desired, a scale control board, and various precautions with regard to cold junctions, etc., must be adopted.

Unfortunately, although the temperature at which a metal is cast is admitted to be of such great importance, yet there is no really satisfactory way of determining the temperature of the molten metal. The conditions, especially where a large crucible is used, make it practically impossible to insert a pyrometer into the metal, and the readings obtained with radiation or optical pyrometers are not consistent, owing to variations in the quality and quantity of the slag and the frequently great divergence from black-body conditions.

The closed-tube radiation pyrometer can be safely used when small crucibles are employed; the thermocouple also, if protected by an outer salamander tube, may be employed for molten brass.

The greatest field for the application of pyrometers lies in the heat treatment of metals, where the success of a pyrometer installation depends almost entirely on the mounting. Experience shows that, in the case of large furnaces, it is advisable to put the thermometer in the floor of the furnace in the following way: A slot is chopped into the furnace floor and into this a fire-clay tube is grouted, the space surrounding the tube being filled in with fire-clay flush with the bottom of the furnace. The pyrometer is slipped into the tube through the side of the furnace. The weight of the head of the pyrometer is taken by a flanged socket, which is screwed into the protective plating of the furnace, the pyrometer being held to the socket by means of readily removable bolts and nuts. Thus the pyrometer can be introduced between the gas ports of the furnace.

In practically all porcelain works Seger cones are employed to control the firing. Although the information given by them is extremely valuable as showing the maximum temperature attained, yet they fail to show the rate at which a kiln is being heated, and this is frequently of fundamental importance. Thermocouples are best employed for the measurement of the lower or preliminary temperature and radiation pyrometers for higher or finishing temperatures.

THE SALT INDUSTRY OF RUSSIA

It is pointed out in *The Times Russian Supplement*, August 11, 1913, p. 8, that there is a great discrepancy between Russia's salt production and her resources in this respect.

Geological investigation proved long ago that there are in various parts of the Russian Empire untouched deposits of salt, that there are lakes in the Astrakhan province and in Siberia which possess a considerable salt capacity, and that mineral salt can be found in large amounts in the Caucasus and in the Ural Mountains. Vast areas that are suspected to be salt-bearing have up to the present time not yet been surveyed. Oil borings in the Ural Caspian district have within recent years disclosed the presence of hundreds of millions of tons of rock salt in the Gouriev and Emba districts. A recent calculation estimates the salt resources of Russia to be capable of supplying the whole world for centuries with this indispensable commodity. In spite of this fact, the production of salt in Russia hardly covers the comparatively moderate consumption of the Empire.

In 1880, Russia produced no more than 750,000 tons of salt. In 1900, the production had increased to two million tons, and in 1912, the output reached 2 $\frac{1}{4}$ millions.

Nearly half of the Russian salt output is obtained in the lakes of Baskunchak and of the Crimea. Although the lake-salt production is the cheapest, the irregularity of its output induces those engaged in the industry to take a special interest in the product obtainable by boiling and in rock salt.

Salt-boiling is principally applied in the Perm and Slaviansk districts.

It is interesting to note that the Siberian dairy farms are using the Slaviansk and not the Perm salt, which, though nearer the Siberian consumer and obtained by the same process of boiling, is inferior in quality.

The most advanced and promising branch of the Russian salt industry is rock salt, of which 85 per cent is produced in the Bakmut district, in Southern Russia. The average yearly salt output in Bakmut was for 1901-5, 500,000 tons and for 1906-10, 560,000 tons, while in 1912, it reached over 600,000 tons. The production of rock salt is less expensive than preparation by the boiling process.

Russia's production is limited by the internal demand, which is increasing slowly. The use of salt in cattle food is practically unknown to the Russian peasantry, and the chemical industries using it as a raw material are not sufficiently developed.

The salt industry depends much on the State, which is the owner of one-half of the salt-producing areas and a producer of several hundred thousand tons. The State gives leases against a certain royalty of extracted salt, and is entitled to force the firms to sell their whole output to the Government at a fixed price. The rise of the price of salt was the object of special investigation by a Commission in 1911, but up to the present moment the State has not used its right of compulsory pre-emption.

The Amur district, a great fishery centre, and consequently an important consumer of salt, is importing this commodity from Japan, China, and especially from Germany, to the amount of over 500,000 tons.

The salt industry being closely connected with the general industrial development of the country, progress in agriculture and chemical production, as well as the betterment of the economic standard of the population, will necessarily lead to an increased output.

CHEMICAL TRADE OF GERMANY

Consul-General Harris, of Frankfurt on the Main, summarizing a number of German authorities, discusses the progress of the chemical trade of Germany during the past few months and throughout 1912. In connection with the statement made by Mr. Harris as to the progress of Germany's chemical trade, statistics show that the exports of raw chemical products during the first half of 1913, compared with 1912, record an increase of more than \$10,000,000 worth, and reach a total of \$47,000,000. Of colors and dyestuffs, an increase of about \$6,000,000 is noted,

the total for the first six months of the present year being \$36,000,000. Of varnish, lac and putty, the exports amount to nearly \$739,000, and really declined during the six months period. Of ethers, alcohol, etc., the total exports for the first six months of 1913 were over \$5,000,000 worth, a gain of \$1,500,000. Exports of artificial fertilizers show a decline of about \$300,000 in a total exportation of the first six months of \$6,143,000 worth. Of pharmaceutical products, a gain of more than \$2,000,000 is noted for the first six months, the total being \$11,963,000.

Giving some details as to the more important items in Germany's trade with the United States and other countries, and calling particular attention to the trade in fertilizers and explosives, Mr. Harris says:

The items of chief importance in the export trade are chemical raw products and colors and dyestuffs, forming together about three-fourths of the total value. Exports of raw materials during the first half of 1913 showed a gain of about 30 per cent over the corresponding period in 1912, 32 per cent over the January-June portion of 1911, and 110 per cent over the first semester of 1908.

A marked increase was shown also in the various salts, such as chloride of potassium, etc. Belgium, France and Austria-Hungary are the principal countries of destination of these shipments, while for salts to be used for fertilizers, which are also included in the export figures, the United States, Sweden, Russia and Austria-Hungary are the chief customers. The import trade of these salts is so small as to be insignificant.

As purchasers of German aniline and other coal-tar colors, China, England and the United States lead. The total shipments of these colors in the first half of 1913 reached in value \$16,855,000, against \$15,726,000 last year. Imports of dyestuffs, with figures much lower than the exports, include certain specialties.

Germany's shipments of artificial fertilizers, while showing a falling off from those of 1912, advanced during the past six years by about 150 per cent. Thomas meal (exports, first half of 1912, \$2,762,000; 1913, \$2,703,000) and superphosphate (exports, first half 1912, \$3,205,000; 1913, \$2,995,000), as by-products of the rapidly increasing mining industries of Germany, furnish the principal items of these exports, which go chiefly to Austria-Hungary, the Netherlands, Russia and Denmark. Imports of artificial fertilizers during the first six months of 1913 amounted to 60 per cent of the exports and came chiefly from Belgium and France.

IMPRESSIONS OF EUROPEAN SEWAGE-TREATMENT METHODS

As Philadelphia's representative, Mr. George E. Datesman, principal assistant engineer of the Bureau of Surveys, visited Europe and made studies of the systems of sewage treatment in cities of Germany, Austria, Holland, Belgium, France and England. The principal conclusions of his report follow:

1. The establishment of government rivers boards to supervise sanitary conditions and works proposed is essential to proper results. The art of sewage disposal apparently has stopped at percolating filters, but an adequate and less costly substitute is anticipated. It is practicable to obtain from properly designed and operated sewage works a clear, odorless, sparkling and non-putrescent effluent from a sewage of extreme concentration, even if it has become septic.

2. Sludge resulting from sewage treatment can be rendered innocuous, practically inodorous and wholly unobjectionable and can be disposed of without nuisance, sometimes profitably. By certain combinations of treatment desired results may be secured at a fraction of the cost of other recognized scientific methods of treatment in satisfactory operation.

3. In the conservation of a water supply, sewage-disposal

systems should bear only their proportion of the cost of treatment. The construction of a properly designed, economical and sanitary collection system is the first essential in sewage disposal.

4. The use of the separate system of sewer conduits has been abandoned as inadequate for urban districts. Polluted streams can be made pure by a system of interceptors to prevent sewage from reaching the streams.

5. Rivers may be made clean and nuisances to sight and smell may be prevented by simple screening or by screening and tankage treatment, provided the diluting volume of river flows and its velocity are sufficient to prevent deposits. Where not used as a water supply the extent to which a river may be used as an oxidizing agent thus offers a problem to be determined.

6. At the present stage of the art there is no process that gives better or cheaper results than the form of tank used at the works of the Emscher Genossenschaft in Germany. Should screening be desired, the so-called Reinsch screens as used at Dresden, Germany, are the most cleanly and efficient of any observed. Experience has proved that adequate tankage treatment is more effective and less costly than the operation of fine screens.

7. Of the bacterial treatments, the percolating filter furnishes the best results both in oxidizing the organic matter and in the removal of putrescibility. The speed of operation is greater than by any other system, with consequent reduced first cost for land areas.

8. When sufficient fats are present in the sewage, they may be profitably recovered from sludge. Drying for fertilizer and fuel use has also proved profitable in some cases.

9. Submerged outlets from disposal works are essential for proper dilution. Disinfection with hypochlorite of lime as a final treatment is not in use either in England or Germany. In the conditions of the rivers in the former country it would not be effective in removing pollution.

ACTION OF ALKALI AND SEA WATER ON CEMENTS

The United States Bureau of Standards has investigated the above subject and has published the results of its investigations in *Bulletin 12*. Since the physical test covered a period of exposure of not to exceed 3½ years, the following conclusions drawn should be considered somewhat tentative:

Portland cement mortar or concrete, if porous, can be disintegrated by the mechanical forces exerted by the crystallization of almost any salt in its pores, if a sufficient amount of it is permitted to accumulate and a rapid formation of crystals is brought about by drying; as larger crystals are formed by slow crystallization, the same results would be obtained on a larger scale, but in greater time if the drying were slow. Porous stone, brick and other structural materials are disintegrated in the same manner. Hence, in alkali regions where a concentration of salts is possible, a dense non-porous surface is essential.

While in the laboratory a hydraulic cement is readily decomposed if intimately exposed to the chemical action of various sulfate and chloride solutions, field inspection indicates that in service these reactions are much retarded if not entirely suspended in most cases, due probably to the carbonization of the lime of the cement near the surface or the formation of an impervious skin or protective coating by saline deposits.

Properly made Portland cement concrete, when totally immersed, is apparently not subject to decomposition by the chemical action of sea water.

It is not yet possible to state whether the resistance of cement to chemical disintegration by sea water is due to the superficial formation of an impervious skin or coating, which is subsequently assisted by the deposition of shells and moss forming a protective coating, or by the chemical reaction of the sea salts with the cement forming a more stable compound without disintegration

of the concrete, or by a combination of both of these phenomena.

Marine construction, in so far as the concrete placed below the surface of the water is concerned, would appear to be a problem of method rather than materials, as the concrete sets and permanently hardens as satisfactorily in sea water as in fresh water or in the atmosphere, if it can be placed in the forms without undue exposure to the sea water while being deposited.

Contrary to the opinion of many, there is no apparent relation between the chemical composition of a cement and the rapidity with which it reacts with sea water when brought into intimate contact.

In the presence of sea water or similar sulfate-chloride solutions, the most soluble element of the cement is the lime. If the lime of the cement is carbonated it is practically insoluble. The quantity of alumina, iron or silica present in the cement does not affect its solubility. The magnesia present in the cement is practically inert.

The change which takes place in sea water when brought into intimate contact with the cement is as follows: The magnesia is precipitated from the sea water in direct proportion to the solubility of the lime of the cement. The sulfates are the most active constituents of the sea water, and are taken up by the cement. Their action is accelerated in the presence of chlorides. No definite sulfate compound was established. The quantity of chlorine and sodium taken up by the cement is so small that no statement can be made as to the existence of any definite chloride or sodium compound formed with the cement.

Metal reinforcement is not subject to corrosion if embedded to a depth of 2 inches or more from the surface of well-made concrete.

ALLOYS OF ALUMINUM

C. H. Iverson, in the *Mechanical Engineer*, discusses the alloys of aluminum with the common and rare metals.

An alloy of 4 per cent nickel has been shown to disintegrate in a very short time after being cast, but the introduction of copper is an advantage. Phosphide of copper added in quantities of 1.5 per cent to a zinc-aluminum alloy containing from 12.5 to 15 per cent zinc gives fluidity to the molten metal. Phosphide of zinc containing 25 per cent phosphorus may be substituted in the proportion of 0.05 per cent. This is one of the best fluxing and cleansing agents the writer knows for all aluminum alloys, and should be added to the molten alloy for a few minutes before pouring by wrapping in paper and plunging to the bottom of the crucible by means of tongs and stirring briskly.

Magnesium-aluminum alloys containing 1 to 10 per cent magnesium are much improved by the addition of 5 per cent zinc, as this addition imparts better wearing properties to the metal and aids in producing homogeneous castings. By the addition of 1 per cent phosphide of copper less oxidation of the metal takes place during the melting operations.

During the last few years metallurgists have been experimenting with some of the rarer metals, and this part of the subject is most interesting. The writer has alloyed aluminum with almost all the rarer metallic elements, such as cerium, neodymium, lanthanum, tantalum, zirconium, and beryllium, and some of these alloys gave most remarkable results even in quantities of only 1 per cent and under. Cerium and beryllium alloys are particularly interesting. An addition of 0.5 per cent of cerium raises the tensile strength of the metal from 4.5 tons per square inch to 10.3 tons per square inch, and gives an elongation of 8.5 per cent on 2 inches. This alloy was placed in sea water and boiled for 60 hours; the sample was carefully weighed before and after the boiling process, and there was no loss in weight. One side of the metal was polished and, after the boiling, was found to be untarnished. An alloy of 2 per cent

beryllium gave a tensile strength of 11.8 tons per square inch with an elongation of 10 per cent on 2 inches. It was of a beautiful silver-white color, and could be hammered out cold into leaf; it also withstood the action of sea water perfectly.

Manganese, titanium, chromium, molybdenum, tungsten, etc., form a very interesting series of alloys, either when alloyed by themselves or in the presence of copper. Titanium and chromium alloys are both affected by sea water and ordinary atmospheric conditions. The former alloy, when polished in the presence of sea water, develops white spots on the metal which, when removed, show deep pit marks on the surface of the metal; this applies to the alloys of chromium as well.

Tungsten has been recommended as being a suitable metal to alloy with aluminum to resist corrosion, but the writer did not find this very satisfactory. An alloy containing 2 per cent copper and 0.5 per cent tungsten rapidly disintegrated under ordinary atmospheric conditions. At least 100 different samples of this alloy were prepared in the varying proportions of 0.2 to 5 per cent pure tungsten alloyed by itself with the aluminum, and also in conjunction with nickel, manganese, copper, etc. The results of some of these were disappointing.

The alloy of zinc and nickel containing 3 per cent nickel and 0.75 per cent zirconium gave extraordinary results as far as tensile strength was concerned, having 12.2 tons per square inch, with elongation 9 per cent on 2 inches. Its behavior in sea water was very extraordinary; it was boiled for 72 hours in sea water, and when tested, after the boiling process, showed only 4 tons per square inch tensile strength. Its fracture was very crystalline, and it was also very brittle. Zirconium 0.75 per cent, when alloyed with aluminum without the presence of nickel, gave the same tensile strength after the boiling process as before, namely, 9.3 tons per square inch.

Molybdenum, when alloyed with aluminum, had the opposite result. An alloy was made containing 1.5 per cent molybdenum with aluminum which, after being boiled in salt water, gave a lower tensile strength than before the boiling; but when the molybdenum was alloyed with the aluminum in the presence of copper in the proportions of molybdenum 1.5 per cent and copper 1.5 per cent, the tensile strength of the metal after the boiling process was the same as originally.

WATERPROOFING OF CONCRETE STRUCTURES

CONCLUSIONS OF COMMITTEE ON WATERPROOFING MATERIALS OF THE AMERICAN SOCIETY OF TESTING MATERIALS

While the committee has not arrived at sufficient conclusions to formulate definite specifications for making concrete structures waterproof, certain results have been reached which may be of assistance in securing impermeable concrete.

In the laboratory and under test conditions using properly graded and sized coarse and fine aggregates, in mixtures ranging from 1 cement, 2 sand and 4 stone to 1 cement, 3 sand and 6 stone, impermeable concrete can invariably be produced. But the reverse often obtains in actual construction, permeable concretes being found even with 1 cement, 2 sand and 4 stone mixtures and these are of frequent occurrence where the quantity of the aggregate is increased. This the committee attributes to defective workmanship, to use of imperfectly sized and graded aggregates, use of excessive water and lack of proper provision to take care of expansion and contraction.

Properly graded sands and coarse aggregates are rarely, if ever, found in nature in sufficient quantities to be available for large construction, and the effect of poorly graded aggregates in producing permeable concrete is aggravated by poor and inefficient field work; it is seemingly a commercial impossibility on large construction to obtain workmanship even approximating that found in laboratory work. In consequence of these conditions substances calculated to make the concrete

more impermeable—either incorporated in the cement or added to the concrete during mixing—are often used.

The committee has investigated a sufficient number of these special waterproofing compounds as well as certain very finely divided mineral products, to form a general idea of the different types.

The majority of patented and proprietary compounds tested have little or no immediate or permanent effect on the permeability of concrete and some are even injurious. The permanent effect of such additions, if dependent on the action of organic compounds, is very doubtful. In view of their possible effect upon the early strength and durability of concrete after considerable periods, no integral waterproofing material should be used unless it has been subjected to long-time practical tests under proper observation to demonstrate its value, and unless its ingredients and the proportion in which they are present are known. In general, more desirable results are obtainable from inert compounds acting mechanically than from active chemical compounds whose efficiency depends on change of form through chemical action after addition to the concrete.

Assuming average quality as to size of aggregates and reasonably good workmanship in the mixing and placing of the concretes, the addition of from 10 to 20 per cent of very finely divided void-filling mineral substances may be expected to result in the production of concrete which under ordinary conditions of exposure will be found impermeable, provided the work joints are properly bonded and cracks do not develop on drying, or through change in volume due to atmospheric changes, or by settlement.

In large construction, no matter how carefully the concrete itself has been made, cracks are apt to develop, due to shrinkage in drying out, expansion and contraction under change of temperature and moisture content and through settlement. Hence, it is often advisable on important construction to anticipate and provide for the possible occurrence of such cracks by external treatment with protective coatings. Such coating must be sufficiently elastic and cohesive to prevent the cracks extending through the coating itself. The application of merely penetrative void-filling liquid washes will not prevent the passage of water due to cracking of the concrete.

While some penetrative washes may be efficient in rendering concrete waterproof for limited periods, their efficiency may decrease with time and it may be necessary to repeat such treatment. The first effort, therefore, should be made to secure a concrete that is impermeable in itself, and penetrative, void-filling washes should be resorted to only as a corrective measure.

While protective extraneous bituminous or asphaltic coatings are unnecessary, so far as the major portion of the concrete surface is concerned, provided the concrete is impermeable, they are valuable as a protection where cracks develop in a structure. It is therefore recommended that a combination of inert void-filling substances and extraneous waterproofing be adopted in especially difficult or important work of any nature. Protective bituminous or asphaltic coatings are often subject to more or less deterioration with time, and may be attacked by injurious vapors or deleterious substances in solution in the water coming in contact with them. The most effective method for applying such protection is either the setting of a course of impervious brick dipped in bituminous material into a solid bed of bituminous material or the application of a sufficient number of layers of satisfactory membranous material cemented together with hot bitumen.

Their durability and efficiency are very largely dependent on the care with which they are applied. Such care refers particularly to proper cleaning and preparation of the concrete to insure as dry a surface as possible before application of the protective covering, the lapping of all joints of the membranous layers, and their thorough coating with the protective material.

The use of this method of protection is further desirable because proper bituminous coverings offer resistance to stray electrical currents.

Of course, no addition of waterproofing compounds or substances can be relied upon to counteract completely the effect of bad workmanship, and the production of impermeable concrete can be hoped for only where there is determined insistence at all times on good workmanship on all structures.

FULLER'S EARTH

The United States Bureau of Mines has just issued a pamphlet (Bulletin No. 21) by Charles L. Parsons, on Fuller's Earth.

Dr. Parsons states that "The United States produces all of the fuller's earth used for refining petroleum within its borders. On the other hand, most of the fuller's earth used in bleaching edible oils has been imported from England. Recently a few of the refiners of cottonseed oil have begun to utilize domestic fuller's earth, whereas others have been unable to substitute it successfully for English earth in their practice. Many samples of American earth distinctly superior in bleaching powder to the English earth have come to the attention of the Bureau of Mines. For these reasons an investigation of the mining, preparation, and use of fuller's earth in this country, especially in its application to edible oils, was conducted in order to ascertain why our own raw material has been deemed inapplicable to our needs.

"During the calendar year 1912, according to figures of the United States Geological Survey, there were imported into the United States 1,970 tons of unground fuller's earth, valued at \$11,619, and 17,139 tons of ground fuller's earth, valued at \$133,718, these values being based on the wholesale market price at the port of origin. The addition of transportation charges, commissions, etc., make the price to the American refiner \$14.50 to \$16 per ton. According to the latest figures compiled by the United States Geological Survey, the United States in 1912 produced 32,715 tons of fuller's earth, valued at \$305,522 or \$9.34 per ton, at the mine. Most of this domestic production was from three plants in Florida and one in southwestern Georgia and was used almost wholly for decolorizing petroleum. A small amount from other localities was used in the refining of edible oils. No figures definitely differentiating fuller's earth from other clays are kept in regard to our exports, but it is certain that several thousand tons of domestic earth were exported to Germany, and it is also true that German refiners of edible oils have used and are using large quantities of American fuller's earth and have a higher appreciation of its merits than our own refiners.

"As a result of the investigations made, the Bureau of Mines believes that the United States has fuller's earth far better suited for refining edible oils than any imported, and that to assure the almost universal use of this earth by American refiners there is required only a careful and intelligent technical control of the preparation of the output and its application to the bleaching of oils."

NEW CHEMICAL PROCESS FOR FIBER

A new process of manufacturing cellulose has been worked out by Dr. J. König: Balsam, fir, pine, spruce, beech and oak woods, as well as spun fibers, may be transformed into a very fine, easily bleachable cellulose, with a cattle feed substance residue, and the elimination at the same time of the waste liquor troubles. The *Journal of the Society of Chemical Industry* (Oct. 15, 1913, p. 939) states that the disintegrated wood or other fibrous material is steamed with four to five times its weight of a 3 to 5 per cent solution of ammonia under a pressure of 2 to 3 atmospheres for five or six hours. The liquor is removed by pressing and the residue is washed with boiling water, the ammonia being recovered by distillation of the liquors, with the addition of lime, if necessary; resins and tannins are obtained

from the residue from distillation. The digested material is next steamed in a similar manner with 4-5 times its weight of 0.4 to 0.6 per cent sulfuric acid for 6-8 hours under a pressure of 1 to 2 atmospheres. The liquors from this treatment contain sugars, the products of the hydrolysis of hemicelluloses and pentosans. These liquors are neutralized either with the lime employed for the recovery of the ammonia or else with powdered limestone and evaporated. The syrup obtained is separated from the calcium sulfate and mixed with dry fodder, chopped hay, brewers' grains, bran, etc., and fed to cattle.

An alternative process consists in steaming with sodium carbonate solution instead of ammonia in the first stage and with hydrochloric acid in the second stage, and mixing the waste liquors from each process so that they neutralize each other; the sodium chloride thus formed is not injurious to the use of the evaporated syrup as a fodder. The exhaustive alkaline and acid treatments do not remove the lignin from the wood, and the residue still contains over 25 per cent of lignin. This, however, is in a form which is readily oxidizable by hypochlorite bleach liquor and the fiber is treated in stages, preferably with dilute sodium hypochlorite, until a residue of bleached cellulose is obtained. It is estimated that 200 pounds of wood yield six pounds of resin (or two to four pounds of tannic acid), fifty pounds of fodder extract rich in sugars and sixty-two to eighty-two pounds of bleached cellulose.

SEWAGE DISPOSAL IN NEW YORK

Number 6 of the *Preliminary Reports* of the Metropolitan Sewerage Commission of New York is the presentment of a study of the collection and disposal of the sewage of the lower Hudson, lower East River and Bay division. Number 7, in the same series, includes the critical reports of G. J. Fowler, of Manchester, England, and J. D. Watson, of Birmingham, England, on the projects of the Commission. These experts agree in advocating the construction of main drainage channels to carry off the sewage of lower New York into the Atlantic Ocean.

EXHAUSTING LAMP BULBS AT HIGH TEMPERATURE

According to *Scientific American* (Oct. 18, 1913), a new method is used for making a vacuum in incandescent lamps or other glass vessels. Heretofore, to eliminate the last traces of moisture and expel air bubbles which adhere to the side of the glass, the lamps have been heated in a special furnace lined with asbestos to equalize the heat to a temperature of 250 or 350° C. But all the air bubbles do not detach even at this heat, and a greater heat cannot be used for fear of softening the glass, when the air pressure would collapse the bulbs. Quite lately the Berlin Allgemeine Company used a vacuum process which permits heating to a higher point and even softening the glass while the lamps are on the air pumps. This is done by placing the lamps in an electric furnace in which a vacuum is made, so that there is scarcely any external pressure on the lamps and they can be heated as high as 500° C. Larger end tubes can be used on the lamps which is better for the vacuum process, but it is a hard matter to fuse off such large tubes for closing, when they have a vacuum inside, as collapsing may occur. An original method is used for this, and a spiral wire electric heater surrounds the tube so that it is softened and can be drawn out while still inside the furnace; the closing off of the lamp is thus effected without air pressure on the outside. Then the surface is allowed to cool down to 350° C. before opening and putting on the atmospheric pressure.

CADMIUM STORAGE BATTERY PLATES

Scientific American (Oct. 18, 1913) reports that Förseke and Aschenback use a new process for making cadmium electrode plates for alkaline accumulators. They use cadmium obtained in finely divided form as a spongy precipitate from a solution

of cadmium salt. They add zinc powder to a solution of cadmium chloride; the precipitated spongy cadmium, mixed with zinc powder and a small amount of oxide of mercury, is spread upon suitable supports for making the battery plates. Such porous cadmium electrodes are used in a caustic soda or potash bath against a nickel electrode. At the first charging by current, the mercury oxide is reduced to the metallic state and the mercury then envelops the particles of cadmium and zinc. On discharging the battery, the zinc dissolves out, while the cadmium becomes oxidized and the mercury remains in the same state and is not affected. The zinc thus remains only temporarily in the mass, and aids in rendering it porous.

FRENCH ALCOHOL PRODUCTION AND USES

Consul General Frank H. Mason, Paris, reports that the French Ministry of Finance has just published some very interesting statistics concerning the production and use of alcohol in France. The total production in 1912 was 87,440,420 United States gallons, as compared with 63,797,165 gallons in 1911. In spite of this enormous production, France received from foreign countries 4,913,571 gallons of pure alcohol and liqueurs. There was a total export trade of 8,321,370 gallons: 40,044,517 gallons were beverages, a small quantity was used for perfume manufacture, and 17,994,896 gallons were denatured. About 2,306,130 gallons were employed for mixing with wine, and 1,490,106 gallons were used in the manufacture of vinegar. Out of the quantity taxed for consumption, 21,905,701 gallons took the form of "eau de vie," or brandy, 5,776,457 gallons were used for absinthe, and 282,557 gallons were used for making perfumery. The remainder was employed in the manufacture of different liquors. Of the 17,994,896 gallons of denatured alcohol 12,662,483 gallons were used for heating and lighting, while 4,113,504 gallons were employed for the manufacture of explosives.

NATURAL GAS USED

According to B. Hill, of the United States Geological Survey, the total estimated consumption of natural gas in the United States in 1912 was 562,203,452,000 cubic feet, valued at \$84,563,957, an average price of 15.04 cents a thousand cubic feet, compared with 512,993,021,000 cu. ft., valued at \$74,621,534, an average price of 14.55 cents, in 1911. The number of domestic consumers supplied with gas in the United States in 1912 was 1,621,557 and the value of gas consumed for domestic purposes amounted to \$50,960,883, while the number of industrial consumers was 15,936 and the value of gas consumed for industrial purposes was \$33,603,074. On the assumption that 28,000 cubic feet of gas equals in heating power 1 ton of coal, the fuel displaced by gas consumed in 1912 was equivalent to approximately 20,000,000 tons of coal.

One feature of particular interest in the year 1912 was the

completion of the pipe line which is to convey natural gas from the Buena Vista Hills, of Kern County, Cal., to consumers in the city of Los Angeles and the surrounding towns.

West Virginia produced 215,785,027,000 cubic feet, valued at \$29,064,968. Pennsylvania was the largest consumer of gas, herself producing to the value of \$22,823,725, but consuming \$26,486,302 worth of gas. West Virginia, on the other hand, consumed only about one-fourth of her output, the balance being piped into other States.

GOLD AND PLATINUM BY THE TON

The production of pig iron in 1912 was 33,802,685 tons of 2,000 pounds each; that of platinum was 1.3 tons. The value of the iron per ton was \$12.44 as against \$1,328,391 per ton for the platinum.

For the sake of convenient comparison and because in commercial practice the various ores and metals are measured by a variety of units such as the long, short and metric ton, flask, avoirdupois pound and troy ounce, the United States Geological Survey has issued a short summary of the "Production of Metals and Metallic Ores in 1911 and 1912," stated in terms of the short ton of 2,000 lbs., considerable of which, however, is derived from imported ores, bullion, etc. A comparison of the production of some of the better known metals may be of interest.

	Short tons	Value
Platinum.....	1.304	\$1,732,221
Gold.....	188.108	113,415,510
Silver.....	4,471.4	80,187,317
Aluminum.....	32,803.0	15,089,380
Quicksilver.....	939.9	1,057,180
Nickel.....	22,421.0	17,936,800
Tin.....	8.4	8,850
Copper.....	734,052.0	242,337,160

PRODUCTION OF PLATINUM

Platinum is now worth \$46 an ounce, against \$20 five years ago. Increased prospecting last year in the United States, however, resulted in a total output of only 721 ounces of crude metal. The world's output is estimated by the Geological Survey in troy ounces as follows:

Country	Ounces		
	1910	1911	1912
Russia.....	275,000	300,000	300,000
Canada.....	30	30	30
New South Wales.....	332	470	500
Colombia.....	10,000	12,000	12,000
United States, domestic crude.....	390	628	721
United States, from foreign and domestic matte and bullion.....	1,000	1,200	1,300
Borneo and Sumatra and other.....	209	...	200
Total.....	286,961	314,328	314,751

Imports of platinum into the United States in 1912 aggregated \$4,503,682 in value.

NOTES AND CORRESPONDENCE

SYRIAN AUTOBURNING LIMESTONE¹

Several months ago, U. S. Consul Whiting, Jerusalem, Palestine, reported (*Daily Consular Reports*, July 21, 1911) upon the self-burning limestone found in the district of Hauran in Syria.

Hauran is a volcanic region lying to the south of Damascus and east of the Upper Jordan. Its surface consists of an elevated plateau made up of fertile plains and barren lava hills. The rich plains are wheat-producing lands.

¹ Paper presented at the 48th meeting of the A. C. S., Rochester, September 8-12, 1913.

A railroad running from Damascus taps this section. Mr. Whiting, who visited this locality and inspected the industry, gives this description:

"The formation occurs in beds, 20 by 30 feet thick, between layers of ordinary limestone. The rock being soft and full of crevices is easily quarried with primitive tools. When freshly quarried the material is black and has a slight odor of petroleum. The rock is broken into small pieces, piled against the quarry wall and then enclosed on 3 sides with a rough wall of the same material, making a rectangular heap 10 feet long by 10 feet wide with a height of 2 feet in front and 6 feet in rear. Small holes or flues are left in the wall for draft. The fire, kindled

by flint and steel is started by a small sheaf of straw. After 12 hours' burning, during which much black and strong smelling smoke is given off, the rock is converted into a lime, white in color, suitable for strong plaster and in every way superior to brush burned lime, and is sold, on account of its low cost of production, at much lower figure. Samples of this rock and its lime were loaned for inspection by the Bureau of Trade, Department of Commerce.

"Another sample of the original rock was procured through the kindness of the U. S. Consul at Jerusalem.

"This Syrian autoburning limestone probably belongs to the asphaltic limestone series of Nebi Musa. These are dark gray, bituminous limestones containing phosphoric acid and holding fossil fish, in layers alternating with variegated red, yellow and white marl" (*Baedecker*, 48, Syria: Geology).

An examination of the samples shows these characteristics: Grayish brown color; no definite odor; soft, resembling hard pressed and dry mud; breaks with a slight conchoidal fracture; specific gravity, 1.74; ignites easily and burns with a smoky flame; can be easily reduced to lime by using a crucible and Bunsen flame. A partial analysis shows:

Loss, drying at 100° C.....	0.12%
Silicious matter.....	2.97%
Iron and alumina oxide and phosphate.....	7.35%
Calcium carbonate.....	67.46%
Magnesium oxide.....	trace
Organic matter.....	21.87%
Total determined.....	99.77%
Sulfur, original limestone.....	1.94%
Nitrogen, original limestone.....	0.68%
Phosphoric oxide, original limestone.....	1.38%

The powdered rock when extracted with chloroform yields 5.37 per cent of a thick brown extract, medium soft, tough and of slight asphaltic odor. When dry-distilled the rock yields 5.28 per cent of a thick, yellowish oil, and alkaline liquor and much foetid-smelling gas. Total loss on distillation is 19.53 per cent.

The heavy, black evil-smelling smoke mentioned by Consul Whiting, and the results of our own small scale experiments suggests the use of a modern kiln whereby valuable by-products (unburned hydrocarbon and ammonia) may be saved.

The original limestone when burned in a calorimeter develops 3220 B. t. u. per pound or a heating value of approximately $\frac{3}{4}$ that of Ohio coal. (Calculations by Chas. E. Kohler, Akron, Ohio.) The softness of the rock together with its proportion of organic matter, phosphoric acid and nitrogen should render it an important soil builder. To such an origin may be due the reason why the Mukra wheat plains of Hauran are regarded as the granaries of Syria.

The rock when finely ground and bolted through a 100-mesh screen gives a *compounding material* suitable for use in black rubber goods. For the purpose indicated it is of value on account of its *mill deportment* and velvety rich colored compound (Ridgway: Color Nomenclature; Plate III, No. 2, deep clove-brown) produced.

CHAS. P. FOX

AERON, OHIO

OBITUARY—JULES OGIER

In the death, at the age of sixty, of Jules Ogier, past president of the Société de Chimie and a member of the Comité Consultatif d'Hygiène Publique de France, France has lost one of her most celebrated forensic and sanitary chemists. After serving as assistant in chemistry at the École supérieure de Pharmacie de Paris, Ogier became assistant to Berthelot at the Collège de France; and in 1883 he was appointed director of the toxicologic laboratory in the medico-legal service of the Paris prefecture of police.

Ogier is best known for his work in public hygiene, which included investigations pertaining to the introduction of water into a number of the large cities of France, the purification of water, the disposal of the sewage of Paris, and the substitution of zinc white for white lead. He was the author of thirty volumes of judicial reports and of the well-known "Traité de Chimie Toxicologique," which appeared in 1899.

W. A. HAMOR

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

SIXTH ANNUAL MEETING, NEW YORK, DECEMBER 10-13, 1913

PROGRAM OF PAPERS

Meetings to be held at The Chemists' Club.

Presidential Address. DR. T. B. WAGNER.

Sanitary Control of the City of New York. ERNST J. LEDERLE.

A Practical Road to the Standard Catalogue. W. M. GROSVENOR.

The Commercial Applications of Ozone. A. VOSMAER.

The Sweetland Filter Press (Lantern Slides and Small Working Model). E. J. SWEETLAND.

A New Filter Press. ALFRED BURGER.

Other papers to be presented—titles not given.

Members will attend the joint meeting of the American Chemical Society, the Society of Chemical Industry and the American Electrochemical Society at the Chemists' Club. Topic of meeting: "The Welfare of Employees in Factories."

EXCURSIONS

Barber Asphalt Paving Company, Maurer, N. J.

Balback Smelting and Refining Company, Newark, N. J.

Sanitary Utilization Company at Barren Island.

Willard Parker Hospital Group of Laboratories, Department of Health of New York City.

Hanson & Van Winkle Company.

Electro-plating and Experimental Plant, Newark, N. J.

Crucible Steel Company of America, Atha Works, Newark, N. J.

Chemical Engineering Laboratories at Columbia University.

Johns Manville Asbestos Company Plant, South Amboy, N. J.

ORTHO-TOLIDINE AS A REAGENT FOR THE COLORIMETRIC ESTIMATION OF SMALL QUANTITIES OF FREE CHLORINE—A CORRECTION

In the article under the above title, *THIS JOURNAL*, 5, 915, in the table at the top of p. 917, only the third or final color in each case refers to a precipitate, the other colors referring to clear solutions.

S. J. HAUSER

BOOK REVIEWS

Industrial and Manufacturing Chemistry: Organic. By GÖEF-FREY MARTIN (assisted by fourteen specialists). New York, D. Appleton & Co., 1913. Large octavo, xx + 726 pp.

Martin states in his preface that this book embraces both British and American practice and that his aim as editor has

been to cover the whole range of subjects with which the industrial chemist and manufacturer are usually concerned, and to make a book which will serve either as a text-book or as a work of reference.

The book is divided into twenty-three sections as follows: The Oil, Fat, Varnish and Soap Industry, 139 pages; The Sugar

Industry, 35 pages; The Starch Industry, 12 pages; The Cellulose Industry, 32 pages; Fermentation Industries, 104 pages; The Charcoal and Wood Distilling Industries, 14 pages; The Turpentine and Rosin Industry, 8 pages; Industrial Gums and Resins, 8 pages; The Rubber Industry, 16 pages; The Industry of Aliphatic Chemicals, 20 pages; The Illuminating Gas Industry, 26 pages; Industry of Coal Tar and Coal Tar Products, 24 pages; Industry of the Synthetic Coloring Matters, 44 pages; The Industry of Natural Dyestuffs, 6 pages; The Ink Industry, 8 pages; The Paint and Pigment Industry, 18 pages; Textile Fiber, Bleaching and Water-Proofing Industry, 16 pages; The Dyeing and Color-printing Industry, 34 pages; The Leather and Tanning Industry, 28 pages; Glue, Gelatine and Albumen Industry, 8 pages; The Industry of Modern Synthetic and Other Drugs, 18 pages; The Modern Explosives Industry, 34 pages; The Industry of Photographic Chemicals, 10 pages.

Milk, cheese, condensed milk and milk powders are discussed in the section on the fat industries. Except for incidental mention in connection with fats and gelatin, no account is given of the industry of slaughtering and meat packing, which, according to the U. S. Census, is the largest manufacturing industry in this country. Except for sugar and fat the food industries, generally, are inadequately treated, the author apparently not realizing to what extent these industries are now coming under chemical control.

As is to be expected in a work consisting of a collection of chapters written by different persons, the text is of uneven quality. Some of the chapters are well written and give a good conception of the industries described; others are little more than catalogues of the materials and products of the industry. At the beginning of each chapter is given a short bibliography, usually confined to book titles and not extending to periodical literature. In those sections in which manufacturing processes are described there are numerous good cuts, and among these it is a pleasure to find several which appear to be new.

On the whole, the work does not seem to be sufficiently well-balanced or well-digested to make a satisfactory text-book, but it appears well worthy of a place on the reference shelf.

H. C. SHERMAN

Chemistry of the Oil Industries. By J. E. SOUTHCORBE, M.Sc., chief chemist of the Henry Wells Oil Co., Salford; lecturer on oils and fats, Royal Salford Technical Institute, etc. (Van Nostrand, 1913.)

This book seems destined to be popular as its two hundred pages run nearly the whole gamut of the oil industry, embracing petroleum, shale oil, waxes, animal and vegetable oils and their products, coal tar oils receiving little mention.

Our main utterance is not against, but because of this book. In the past twelve months or so a number of text-books on oils have appeared, such as the 1913 edition of Holde, *Untersuchung der Kohlenwasserstoffe und Fette*, which covers in a somewhat more comprehensive manner the field treated by Southcombe. Then there is a little book by Gurwitsch, *Wissenschaftliche Grundlagen der Erdölverarbeitung*, treating the subject of petroleum in an admirable way. These with Rakusin and several others afford plenty of publications from the German or Russian standpoint. Through an American publisher, two English writers, Bolton and Revis, have just issued a book on Fatty Foods. A recent book by Simmons and Mitchell on Edible Oils and Fats is also a terse contribution to the subject.

In short, we have plenty of text-books or manuals from authors on the other side, who are largely unfamiliar with the practice in this country and often do not attempt any description of American methods. Practically no books treating of American practice in a satisfactory and comprehensive way exist and one must hunt up chapters in various treatises in order to secure the rather meagre material available. The appearance of another

American publication by a writer from abroad, leads us to plead for a book on the oil industry written by American experts. A treatise in the style of Rodger's *Industrial Chemistry*, but devoted solely to petroleum, coal tar, animal and vegetable oils and waxes, prepared in collaboration by American chemists would be most welcome and American publishers undoubtedly would be assured of much better sales for such a book than for those from English writers.

But to return to Southcombe, the first chapter entitled *Introductory Organic Chemistry*, although giving one a "Cook's Tour" through the subject, is really admirably written. The chapters on mineral and shale oils are rather brief, but give a general notion of present-day theory and practice. Benzene is described as having a boiling point of 85° C. In the preface, Southcombe intimates that colloid chemistry is one of the important considerations involved in the present study of oils, but it appears that he has not discussed this phase of the subject to a sufficient extent in view of the striking developments reported. Although he describes the formalite reaction, he does not mention the Rakusin phenomenon. The subject of refined petroleum is hardly adequately discussed.

Chapter III on the sources of saponifiable oils treats, at unexpected length, the subject of extraction with solvents; or rather the solvents themselves, the chemical properties of the latter being described largely to the exclusion of a discussion of their operative qualities. For example, data on the preparation of tetrachloride of carbon, its specific gravity, boiling point, etc., is given, but no mention is made of the technically important fact that tetrachloride of carbon decomposes in the presence of water yielding acid which attacks the apparatus in which extraction is being conducted. Nor is it stated that ethylene trichloride which is now on the market and used not inconsiderably is generally more satisfactory than the tetrachloride on the score of stability.

The chapter which follows on technical methods of removing impurities from crude oils and fats in some respects is deficient from the standpoint of American practice. Only one or two lines are given over to fuller's earth, while considerable space is devoted to bichromate bleach and similar bleaches of lesser importance. Deodorizing fatty oils by treatment with superheated steam in partial vacuum is quite too general a method to fail of mention.

In Chapter V the topic of unsaturated acids is incomplete for a book published in the year 1913 because only the merest reference is made to the hardening of fats and fatty acids by hydrogenation. This generally regarded epoch-making development is alluded to on page 87 as follows: "A number of patents have been taken out purporting to effect the reduction by passing hydrogen gas over mixtures of the acids and finely-divided nickel which acts as a hydrogen carrier or catalyst." In view of the wide-spread adoption of hydrogenation methods we regard this brief mention as inadequate.

The chapter on Analytical Methods is on the whole commendatory, although some tests, such as that given for the detection of rosin oil, could be elaborated to advantage. The prevalent use of electric heating appliances makes it nowadays unfashionable to illustrate Soxhlet extraction apparatus with a Bunsen burner. On pages 134 135 photo-micrographs of cholesterol and phytosterol could well supplement the free hand sketches shown. The determination of melting point and titer is not given sufficient consideration. From Southcombe's discussion of viscosity one would think the only method for viscosity determination is by the Boverton Redwood Viscosimeter, which, although a widely used instrument in England, is not in general use in this country. No other viscosimeter is described and the treatment of the subject is regarded as incomplete. The subject of colorimetry receives no consideration.

Polymerized and blown oils and also Turkey red oils are briefly

described under the industrial applications of fats and oils. The distillation of fatty acids (Chapter X) and candle manufacture, soap-making and glycerine (Chapter XI) complete the descriptive part of the book. A few pages of concluding matter on "Scientific and Technical Research on Problems in the Oil and Related Industries" are of considerable interest.

In spite of the foregoing comments the book is highly to be recommended as giving, in a comprehensive form, the important facts connected with this subject, remembering as the author would have us, "that in so small a volume it has been impossible to deal in any way completely with the multitude of facts and theories relative to such an extensive subject, and the object of the work is rather to fill the gap between the elementary textbooks of pure chemistry and the numerous technical treatises and monographs of a highly specialized character."

CARLETON ELLIS

Explosives: A Synoptic and Critical Treatment of the Literature of the Subject as Gathered from Various Sources. By H. BRÜNSWIG. Translated and Annotated by Charles E. Munroe and Alton L. Kibler. 350 pp. Illustrations and Tables. John Wiley and Sons, New York, 1912. Price, \$3.00.

The appearance of Dr. Brünswig's book in Germany in 1909 attracted widespread attention and much favorable comment. As stated in the preface the object of the book is to gather together the facts recorded in the literature of explosives, arrange them in accordance with physical chemical views, and make a survey of the present status of the chemistry of explosives and its most important aims. Although many volumes have been written on the subject of explosives from a technical standpoint, it remained for Dr. Brünswig to collect the various data pertaining to the scientific study of the subject and arrange them in an exact science of the chemistry of explosives.

Primarily intended as a text-book, an extended exposition of intricate mathematical problems related to the subject has been omitted for the benefit of those technical workers who do not possess an advanced mathematical knowledge but who are interested in a scientific treatment of explosives. On the other hand, all strictly technical terms have been avoided that the book may be intelligible to those who have only a theoretical and scientific knowledge of the subject. In adapting his book to these two classes of readers, Dr. Brünswig has produced a work which is readable by all classes interested in the subject—and yet at the same time is thoroughly scientific and more deeply technical than at first reading would appear.

Dr. Brünswig is peculiarly fitted to produce such a work as has been described above. His connection with the "Zentralstelle für wissenschaftlich-technische Untersuchungen" at Neubabelsberg has brought him into close contact both with the practical and technical use of explosives on the one hand, and the theoretical and scientific investigations which have been conducted, on the other. In collecting his data he has not, by any means, confined himself to the German sources of literature but has laid the chemical literature of all countries under contribution. The German source of the book should therefore not deter any one from its use.

The book is divided into two parts. Part I, which is by far the larger and more important, deals with a scientific discussion of the laws and behavior of explosive systems. The following subjects are discussed in detail in as many chapters: Conditions governing explosive reactions, including a discussion of exothermal reactions, sensitiveness and initial impulse; velocity of explosive reactions, including discussions of the influence of temperature, pressure and catalytic agents, both on initial velocity and velocity of propagation; pressure developed by explosions, with rate of increase and maximum pressure; temperature of explosions; gases from explosive reactions, with influence

of pressure and temperature; explosions by influence, with both velocity and intensity of explosive impulse; and the flame of an explosion.

Part II describes the characteristics of particular explosives, which are divided into propellants and blasting explosives. This part of the work is of necessity treated briefly in order to cover the whole ground. The details of manufacture are, of course, not described. The treatment is confined to a brief historical sketch of each explosive, its general properties, nature and purpose and an indication of the method of its manufacture.

We have seldom seen a book so thoroughly indexed. A table of contents gives at a glance the general arrangement of the subjects treated. An exhaustive index, both of authors and subjects, enables the reader to turn at once to any fact which the book contains. An idea of the large amount of literature laid under contribution in the preparation of the book is gleaned from the index of authors which covers fourteen pages. Throughout the book references to the original literature are cited so that the book may be used as a basis for an extended investigation into any line connected with explosives.

The translators have done their work remarkably well. It is not a literal translation of the German form of speech and sentence, but a sympathetic transference of thought from the German into the English channels. At the same time the idea of the original is strictly adhered to. A large number of additional references and notes from American sources have been added by the translators and this largely increases its value to American readers.

A. M. COMEY

Allen's Commercial Organic Analysis. Volume VII. By the editors and the following contributors: G. Barger, Vegetable Alkaloids; E. F. Armstrong, Glucosides; G. C. Jones, Non-glucosidal Bitter Principles; A. E. Taylor, Animal Bases; G. Barger, Ptomaines or Putrefaction Bases; J. A. Mandel, Animal Acids; W. A. Davis, Lactic Acid; and Herbert Philipp, Cyanogen and its Derivatives. Fourth edition. Entirely rewritten. Philadelphia, P. Blakiston's Son & Co., 1913. 558 pp. Price, \$5.00.

This edition differs from the former in having been written by several men expert in the particular field, to which the individual chapters are devoted. This ought to be of value, since it is difficult for any one to be so well versed in the whole field of organic analysis as a book of this kind requires. A large portion is descriptive matter rather than consisting of methods of analyses, which will always be of value to the analyst, although it does not conform exactly to the title of the book. The same plan of classification and subjects discussed has been followed, thus making it more convenient for those already familiar with the older edition. The material has been gotten up very well, and only a few errors were noticed such as on page 206, the definition of amic acids is rather vague, and on page 212 the term phenyl isocyanate is used for phenyl uramino-derivative. On the whole, the book is excellent and ought to receive a hearty welcome by all chemists interested in this field of work.

J. M. NELSON

Natural Rock Asphalts and Bitumens. By ARTHUR DANBY. D. Van Nostrand Co., 1913.

As stated in the preface, the book is written for those who are desirous of obtaining a deeper and clearer insight into the production, properties and uses of asphalts and bitumens, and who "find that such knowledge is inaccessible, owing to the lack of any recent English work dealing with them." This statement is undoubtedly correct if it alludes to publications appearing in Great Britain, but the author apparently overlooks the fact that during the past few years, a number of excellent books dealing with this same subject have been published in the United

States which are quite accessible to the English public. In fact, the author openly states that the two chapters on "American Deposits of Bitumen" have been compiled largely from Mr. Clifford Richardson's work "The Modern Asphalt Pavement."

The book under review is largely a reiteration of what has been published in other works, and contains either little new matter or the results of original research. It is written in a semi-scientific style, and fails to impart even to the lay reader a sufficiently lucid explanation of the physical and chemical properties of the asphalts and bitumens under discussion, to enable him to draw any conclusions as to what purposes they are adapted, and to what not. Reference is made to the hypotheses and conclusions of early writers, which however in view of recent disclosures are no longer tenable. These are presented to the reader as facts bearing on the subject under discussion, and without any explanatory statements. Thus on pages 139 and 140 the terms "petrolene" and "asphaltene" are stated to have originated with Boussingault in 1836, who separated the bitumen into these two bodies by distillation. The author goes on to say that the methods now in vogue for determining petrolene are by distilling the bitumen with water, by solubility in boiling alcohol, or by simply heating to a temperature of 250 to 260° C. and noting the loss in weight. Any one familiar with this subject will know that these alternative methods will fail to give equivalent results, and are at best grossly misleading.

The author's definitions of the terms "Bitumen," "Pitch," and "Asphalt," proposed on page 7 are untenable and at variance with the consensus of opinion. Thus bitumen is defined as "substances which are found in nature * * * which are *completely soluble in carbon bisulfide*, but only partially so in ether, and almost *completely insoluble in alcohol* * * *," and among other varieties are stated to include elaterite and wurtzilite. In this connection it is to be noted, as stated above, that the author recommends that petrolene be determined by the solubility of the material in alcohol. Furthermore, it is a well-known fact that elaterite and wurtzilite are practically insoluble in carbon

bisulfide, and this is borne out on page 117, where the author himself contradicts his previous statement.

The chapter entitled "Tests and Analyses" includes a number of methods which on their face cannot possibly give reliable results. Thus on page 138 it is stated with reference to the determination of the mineral matter in asphalts: "If there are any mineral bodies present mixed with these organic substances, they remain unchanged even when the basin is brought to a constant white heat and that temperature sustained for a long time." This would certainly tend to decompose the limestone (calcium carbonate) which occurs in most of the continental rock asphalts. The method for determining the melting point (page 141) is inaccurate, and manifestly inferior to others in current use. Several methods are recommended for differentiating between asphalts of natural and artificial origin in spite of the fact that authorities have repeatedly questioned their reliability.

The chapters on "The Carrying Out of Rock Asphalt Work" and "The Carrying Out of Rock Asphalt Mastic Work" are quite comprehensive, although the methods described are at variance with the practice in this country. In marked contrast to the rest of the work, the section devoted to rock asphalt mastic work goes into the subject with the minutest detail, both in illustrations and in reading matter. This, however, will scarcely be of practical interest to the American reader.

Upon reading through the book, one cannot help noting the rambling way in which it is written, and the many digressions from the main theme.

HERBERT ABRAHAM

CORRECTION

Liquid Air—Oxygen—Nitrogen. By GEORGES CLAUDE.

The price of \$1.50 quoted in our review of this book (THIS JOURNAL, 5, 876) was a mistake. The price given by Blakiston's Son & Co., Philadelphia, is \$5.50.

NEW PUBLICATIONS

By D. D. BEROLZHEIMER, Librarian The Chemists' Club, New York

Ammonia, The Oxidation of, to Nitric and Nitrous Acids. By ED. DONATH AND A. ANDRA. 8vo. 110 pp. Price, \$1.25. F. Enke, Stuttgart. (German.)

Analysis, Industrial Organic. By PAUL S. ARUP. Sm. 8vo. Price, \$2.00. J. & A. Churchill, London.

Analysis, Qualitative. By F. P. TREADWELL. 3rd English ed. 8vo. 534 pp. Price, \$3.00. John Wiley & Sons, New York. (Translation.)

Analysis, Quantitative, by Electrolysis. By ALEXANDER CLASSEN. 5th ed. 8vo. 308 pp. Price, \$2.50. John Wiley & Sons, New York. (Translation.)

Analysis, Quantitative Chemical, Text Book of. By ALEX. C. CUMMING AND SYDNEY A. KAY. Demy 8vo. 396 pp. Price, \$2.00. Gurney & Jackson, London.

Analysis, Quantitative Inorganic, A Treatise on. By J. W. MELLOR. 8vo. 778 pp. Price, \$7.50. Chas. Griffin & Co., New York.

Catalysis in Organic Chemistry. By PAUL SABATIER. 8vo. Price, \$2.50. Paris, 1913. (French.)

Celluloid. By PIEST, STICH AND VIEWEG. 8vo. Price, \$2.25. Wilhelm Knapp, Halle.

Chemistry, Inorganic and Organic. By CHARLES L. BLOXAM. 10th ed. 8vo. Price, \$5.25. J. & A. Churchill, London.

Chemistry, Textbook of. By WILLIAM A. NOYES. 8vo. 602 pp. Henry Holt & Co., New York.

Cyanides, The Chemical Processes of Extracting Silver Ores with. By EMIL KUEHN. 8vo. 108 pp. Price, \$1.50. Wilhelm Knapp, Halle. (German.)

Distillation, The Modern Art of. By E. WALTER. 3rd ed. 8vo. 142 pp. Price, \$2.25. G. Harnecker, Frankfurt a/O. (German.)

Food Inspection and Analysis. By ALBERT E. LEACH AND ANDREW L. WINTON. 3rd ed. L. 8vo. 1001 pp. Price, \$7.50. John Wiley & Sons, New York.

Fuller's Earth. By CHARLES L. PARSONS. 8vo. 38 pp. U. S. Bureau of Mines, Bulletin 71.

Furnaces, Electric, in the Iron and Steel Industry. By W. RODENHAUSER AND I. SCHOENAWA. 8vo. 419 pp. Price, \$3.50. John Wiley & Sons, New York. (Translation.)

Inflammability of Coal Dust, A Laboratory Study of. By J. C. W. FRAZER, E. J. HOFFMAN AND L. A. SCHALL, JR. 8vo. 58 pp. U. S. Bureau of Mines, Bulletin 50.

Inorganic Chemistry, Handbook of the Methods of. I. By ARTHUR STAEBLER. Vol. 5. L. 8vo. Price, \$7.00. Veit & Co., Leipzig.

Metals: The Quantitative Methods for the Examination of Molybdenum, Vanadium, Tungsten, their Ores, Steels, Alloys and Compounds. By H. MENNICKE. 8vo. Price, \$2.25. M. Krayn, Berlin. (German.)

Milk, Its Production, Examination, Handling and Use. By H. TIEMANN. 8vo. 144 pp. Price, \$1.50. H. Reichenbach, Leipzig. (German.)

Organic Substances, Table of the Most Important, Arranged According to Melting Points. By R. KEMPF. 8vo. Price, \$1.50. F. Vieweg & Sohn, Brunswick. (German.)

Power for Factories, Determination of the Cheapest Source of. By KARL URBAIN. 2nd ed. 8vo. Price, \$1.25. Julius Springer, Berlin. (German.)

Pumping and Hydraulic Machinery, Modern. By EDWARD BUTLER. 8vo. 473 pp. Price, \$4.50. Chas. Griffin & Co. London.

Rare Earths, The Use of. By C. R. BOEHM. 8vo. \$1.25. Veit & Co. Leipzig. (German.)

Rubber: Caoutchouc and Gutta Percha Resins. By G. HILLEN. 8vo. 95 pp. \$1.25. M. Drechsel, Berne.

Rubber, The Preparation of Plantation. By SIDNEY MORGAN. 8vo. Price, \$2.75. Rubber Growers' Association, London.

Spectral Chemistry, Introduction to. By G. URBAIN. 8vo. 215 pp. Price, \$2.50. Th. Steinkopff, Dresden. (German.) (Translation.)

Sugars and Their Simple Derivatives, The. JOHN E. MACKENZIE. Demy 8vo. 258 pp. Price, \$2.00. Gurney & Jackson, London.

- Sulfurous Acid and its Compounds with Aldehydes and Ketones.** By W. KIEP, *et al.* 8vo. 469 pp. Price, \$3.00. Kaiserliches Gesundheitsamt, Berlin (German).
- Textil Fibers, Textbook of the Chemical Technology of the.** Vol. I. By G. VON GEORGEVITSCH. 4th edition. 8vo. Price, \$3.75. E. Gernsheim, Leipzig (German).
- Water Bacteriology, Elements of, with Special Reference to Sanitary Water Analysis.** By S. C. PRICOTT AND C. E. A. WINSLOW. 3rd ed. Sm. 8vo. 318 pp. Price, \$1.75. John Wiley & Sons, New York.
- Water Purification and Sewage Disposal.** By J. TILLMANS. 8vo. 143 pp. Price \$2.00. D. Van Nostrand Co., New York.
- Waters, Underground, for Commercial Purposes.** By FRANK L. RECTOR. 12mo. 97 pp. Price, \$1.00. John Wiley & Sons, New York.

RECENT JOURNAL ARTICLES

- Acetone, The Determination of.** By W. M. MARRIOTT. *Journal of Biological Chemistry*, Vol. 16, 1913, No. 2, pp. 281-291.
- Alcohol and Alcoholometry, Bibliography of the Literature of.** By E. C. McILVEY. *Bulletin of the Bureau of Standards*, Vol. 9, 1913, No. 3, pp. 436-474.
- Alcohol, Ethyl, and its Mixtures with Water, Density and Thermal Expansion of.** By N. S. OSBORNE, E. C. McKILVEY and H. W. BEARCE. *Bulletin of the Bureau of Standards*, Vol. 9, 1913, No. 3, pp. 327-435.
- Ammonia, The Inorganic Synthesis of.** By OTTOKAR SERPEK. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 83, pp. 606-609.
- Calcium, Gravimetric Determination of, as Oxalate.** By S. GAY. *Chemiker Zeitung*, Vol. 37, 1913, No. 131, pp. 1337-1338.
- Chlorophyll.** By R. WILLSTAETTER. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 89, pp. 641-645.
- Coals of Canada, The.** ANONYMOUS. *Bulletin of the Imperial Institute*, Vol. 11, 1913, No. 3, pp. 496-513.
- Condensation Product, a Phenol-Formaldehyde; Juvelith.** By FRITZ POLLAK. *Chemiker Zeitung*, Vol. 37, 1913, No. 121, pp. 1233-1234.
- Dyeing of Wool, Studies in the.** By J. MERRITT MATTHEWS. *Canadian Textile Journal*, Vol. 30, 1913, No. 11, pp. 347-349.
- Furnaces, Electric, Their Design, Characteristics and Commercial Application.** By W. MCA. JOHNSON AND G. N. SIEGER. *Metallurgical and Chemical Engineering*, Vol. 11, 1911, No. 11, pp. 643-648.
- Gas, Blast-Furnace, The Cleaning of.** By W. A. FORBES. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 82, pp. 247-251.
- Gas, Oil.** By I. B. JONES. *American Gas Light Journal*, Vol. 99, 1913, No. 18, pp. 273-279 and 282.
- Mercury, Occurrence, Distribution and Uses of.** ANONYMOUS. *Bulletin of the Imperial Institute*, Vol. 11, 1913, No. 3, pp. 479-495.
- Metals and Alloys, Coloring Non-ferrous.** By E. F. LAKE. *Scientific American Supplement*, Vol. 76, 1913, No. 1973, pp. 266-269.
- Milk, Qualitative Determination of Fat in.** By WALTER L. CROLL. *Biochemical Bulletin*, Vol. 2, 1913, No. 8, pp. 509-518.
- Nitrocelluloses, The Examination of, under the Polarization Microscope.** By HANS AMBRONN. *Kolloidchemische Beihfte*, Vol. 13, 1913, No. 4, pp. 200-207.
- Ores: The Scientific Foundations of the Roasting Processes.** By RUDOLF SCHENCK. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 87, pp. 646-652.
- Pyrophoric Metals.** By W. DEDERICHS. *Welt der Technik*, Vol. 75, 1913, No. 19, pp. 370-371.
- Silk, The Manufacture of Artificial, from Cotton.** By H. R. CARTER. *Cotton*, Vol. 78, 1913, No. 1, pp. 28-31.
- Steel Making, Fuel Possibilities in.** By WILLIAM WHIGHAM. *Coal and Coke Operator and Fuel Magazine*, Vol. 32, 1913, No. 1, pp. 595-598.
- Steel, The Influence of Various Elements on the Absorption of Carbon by.** By ROBERT R. ABBOTT. *Bulletin of the American Institute of Mining Engineers*, 1913, No. 82, pp. 2389-2400.
- Steel, The Over-Oxidation of.** By W. R. SHIMER AND F. O. KICHLINE. *Industrial World*, Vol. 47, 1913, No. 42, pp. 1255-1257.
- Stones: The Modern Manufacture of Artificial Marble.** By MAURICE DE KEGHEL. *Revue de Chimie Industrielle*, Vol. 24, 1913, No. 286, pp. 245-251.
- Sugar: Recent Developments in Evaporation.** By ALFRED L. MEBRE. *Louisiana Planter*, Vol. 51, 1913, No. 18, pp. 306-310.
- Titanium, Determination of, by Titration with Methylene Blue.** By BERNHARD NEUMANN AND ROBERT K. MURPHY. *Zeitschrift fuer angewandte Chemie, Aufsatzteil*, Vol. 26, 1913, No. 83, pp. 613-616.
- Towers, Absorption and Reaction, for Chemical Works.** By RUDOLF HEINZ. *Chemical Engineering and the Works Chemist*, Vol. 3, 1913, No. 29, pp. 273-277.
- Zinc, Condensation of, Gas to Liquid, in the Presence of Inert Gas.** By CLERC. *Metallurgical and Chemical Engineering*, Vol. 11, 1913, No. 11, pp. 637-640.

RECENT INVENTIONS

By C. L. PARKER, Solicitor of Chemical Patents, McGill Building, Washington, D. C.

Treatment of Metal-bearing Solutions. E. A. Ashcroft, Sept. 2, 1913. U. S. Pat. 1,071,856. Zinc is obtained from solution by adding calcium cyanamid and heating the mixture.

Iron and Steel Refined by Ferrochromium Alloy. J. Buchel, Sept. 2, 1913. U. S. Pat. 1,071,873. An expeditious and uniform distribution of the chromium introduced as ferro-chromium into the bath of the metal under treatment is obtained by adding carbon-free ferrochromium containing a reducing agent.

Cyanogen Compounds, etc. C. E. Acker, Sept. 2, 1913. U. S. Pat. 1,072,373. An impalpable amorphous carbid of some reactive metal such as barium, lithium, calcium, strontium or

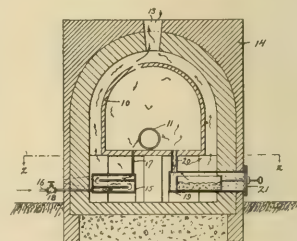
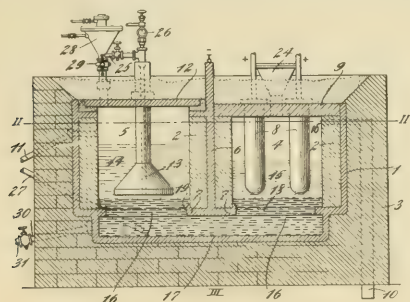
The product of the reaction is dissociated in the presence of an alkali metal, thereby causing the carbon and nitrogen to unite with such alkali metal to form the product sought.

Explosive. J. F. O'Brien, Sept. 2, 1913. U. S. Pat. 1,071,949. The composition contains potassium chlorate, naphthalene, asphalt dissolved in crude oil distillate, powdered carbon, potassium ferrocyanide and silica.

Rust Proofing Iron, Steel, etc. A. Bontempi, Sept. 9, 1913. U. S. Pat. 1,072,904. The metal is subjected to the fumes of a fused non-corrodible material such as zinc or lead while maintained at a temperature above the fusing point but below the fuming point of the coating material. The process may be practiced in a muffle furnace of the character illustrated.

Caoutchouc Substance. C. Harries, Sept. 16, 1913. U. S. Pat. 1,073,116. The composition is produced by subjecting isoprene to the action of sodium.

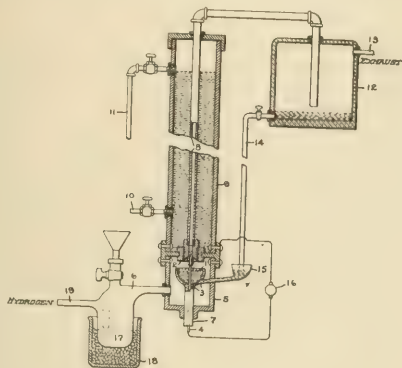
Explosive. J. F. O'Brien, Sept. 16, 1913. U. S. Pat. 1,073,279. The explosive contains potassium chlorate, sodium nitrate, liquid binitrotoluene and sawdust.



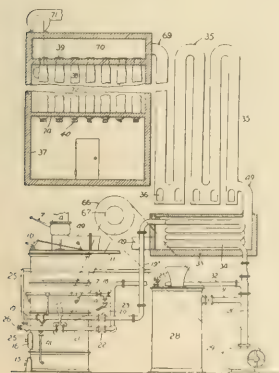
manganese, held in suspension in and diffused through a nitro-geneous salt, is reacted upon by a nitro-geneous reagent such as nitrogen, nitrids or ammonia, at a temperature above 500°.

Portland Cement. J. W. Richards, Sept. 23, 1913. U. S. Pat. 1,073,820. This process is designed to produce Portland cement and iron in a single operation. A charge of iron is made up with the raw materials for producing a lime alumina silicate slag with an excess of limestone sufficient to produce a liquid product having the percentage composition of Portland cement clinker. The charge is heated in a reduction furnace having a basic lining to a sufficient temperature to reduce the ore and to cause the clinker to flow from the furnace in a liquid state.

Electrochemical Process. J. L. R. Hayden, Sept. 9, 1913. U. S. Pat. 1,072,945. This process is stated to be founded upon the patentee's observation that the chemical activity of an electrical arc is not entirely due to the high temperature existing therein but is due in part at least to an electrical effect which is distinct from the purely thermal action of the arc and that



a high temperature in the arc therefore represents a waste of energy. In the process a gaseous mixture to be chemically acted upon is subjected to a low temperature arc formed between a cathode (1) of an easily vaporizable material such as mercury and a perforated anode (2) of some material inert under the conditions, such as copper.

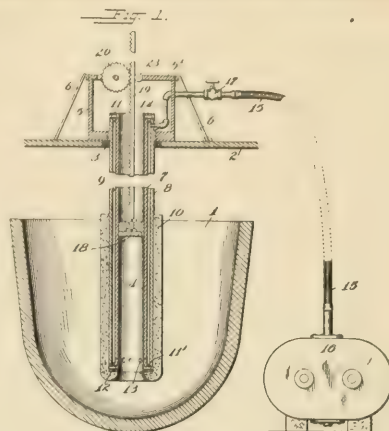


Treating Sulfid Ores.

E. E. Banes, Sept. 16, 1913. U. S. Pat. 1,073,462. Finely pulverized lead sulfid ore is fed continuously into a furnace through the cores of impinging blowpipe flames whereby it is completely volatilized and projected in a volatilized condition into an enveloping oxidizing atmosphere. The resulting fume is drawn off and the white lead sublimate separated.

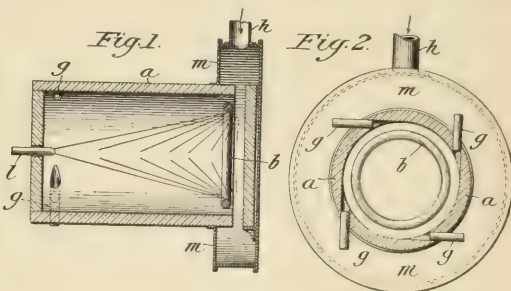
Making Iron and Steel. J. R. Billings, Sept. 23, 1913. U. S. Pat. 1,073,587. Powdered carbon is forced by plunger 18 downward into molten iron contained in the ladle 1. Regulated portions of this carbon escape and rise freely through the mass. Simultaneously with this operation regulated quantities of oxygen are forced through passages 9 and openings 13 into the iron, the quantity of oxygen employed being not greatly in excess of the amount required to effect the complete combustion

of the carbon, with the production of the maximum quantity



of carbon dioxide. The molten metal while heavily charged with carbon dioxide is converted into castings.

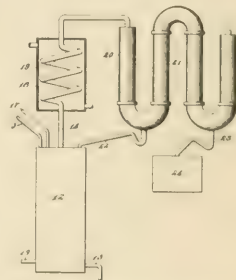
Synthesizing Gases. W. Siebert, Sept. 23, 1913. U. S. Pat. 1,073,823. Electric flame discharges are produced between the rod shaped electrode *l* and the annular electrode *b* by means



of a large current of low voltage per unit distance of separation of the electrodes. The arc is caused to rotate by means of streams of the gases to be acted upon projected into the furnace through the angularly disposed nozzles *g*.

High Concentration of Watery Nitric Acid. H. Pauling, Sept. 30, 1913. U. S. Pat. 1,074,287. Dilute nitric acid to be concentrated enters the reaction column 12 through pipe 16 while sulfuric acid of 80% grade enters through pipe 17. The falling streams are met by a countercurrent of superheated steam which enters the column through pipe 13. In the reaction column the nitric acid is almost completely separated from the water which it contains. The steam is absorbed by the sulfuric acid and the latent heat liberated evaporates the nitric acid which escapes through pipe 14 into the cooling coil 19 from which it passes into condensers 20 and 21. The acid from the condenser 20 may be returned to the reaction column through pipe 22 for further treatment.

The highly concentrated nitric acid which collects in condenser 21 is drawn off through pipe 23. The spent sulfuric acid which contains substantially all of the water originally present in the dilute nitric acid is drawn off through pipe 15 and is concentrated for reuse.



MARKET REPORT

AVERAGE WHOLESALE PRICES OF STANDARD CHEMICALS, ETC., FOR THE MONTH OF NOVEMBER, 1913

ORGANIC CHEMICALS

Acetanilid.....	Lb.	21	@	23
Acetic Acid (28 per cent).....	C.	1.75	@	1.90
Acetone (drums).....	Lb.	14 1/2	@	14 1/2
Alcohol, denatured (180 proof).....	Gal.	33	@	36
Alcohol, grain (188 proof).....	Gal.	2.48	@	2.50
Alcohol, wood (95 per cent).....	Gal.	46	@	48
Amyl Acetate.....	Gal.	2.00	@	2.10
Aniline Oil.....	Lb.	10	@	10 1/2
Benzoic Acid.....	Lb.	23	@	27
Benzol (90 per cent).....	Gal.	21	@	23
Camphor (refined in bulk).....	Lb.	42 1/4	@	44
Carbolic Acid (drums).....	Lb.	8	@	10
Carbon Bisulfide.....	Lb.	6 1/4	@	8
Carbon Tetrachloride (drums).....	Lb.	7 1/4	@	7 1/2
Chloroform.....	Lb.	25	@	35
Citric Acid (domestic), crystals.....	Lb.	55	@	56
Dextrine (corn).....	C.	3.02	@	3.23
Dextrine (imported potato).....	Lb.	6	@	7
Ether (U. S. P., 1900).....	Lb.	14	@	20
Formaldehyde.....	Lb.	8 1/4	@	9 1/4
Glycerine (dynamite).....	Lb.	19 1/2	@	20
Oxalic Acid.....	Lb.	7 1/4	@	7 1/2
Pyrogallie Acid (bulk).....	Lb.	1.20	@	1.40
Salicylic Acid.....	Lb.	25	@	30
Starch (cassava).....	Lb.	3 1/4	@	4
Starch (corn).....	C.	2.24	@	2.90
Starch (potato).....	Lb.	4 1/2	@	5
Starch (rice).....	Lb.	8	@	9
Starch (sago).....	Lb.	2 3/4	@	2 3/4
Starch (wheat).....	Lb.	5 1/4	@	6 1/2
Tannic Acid (commercial).....	Lb.	35	@	36
Tartaric Acid, crystals.....	Lb.	31 1/4	@	32

INORGANIC CHEMICALS

Acetate of Lead (brown, broken).....	Lb.	7 3/4	@	8
Acetate of Lime (gray).....	C.	2.00	@	2.05
Alum (lump).....	C.	1.75	@	2.00
Aluminum Sulfate (high-grade).....	C.	1.25	@	1.75
Ammonium Carbonate, domestic.....	Lb.	8	@	8 1/2
Ammonium Chloride, gray.....	Lb.	5 1/8	@	6 1/8
Aqua Ammonia (drums) 16°.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	3	@	4
Barium Chloride.....	C.	1.75	@	2.00
Barium Nitrate.....	Lb.	5 1/4	@	5 1/2
Barytes (prime white, foreign).....	Ton	19.00	@	23.50
Bleaching Powder (35 per cent).....	C.	1.25	@	1.30
Blue Vitriol.....	Lb.	5	@	5 1/4
Borax, crystals (bags).....	Lb.	3 3/4	@	4 1/4
Boric Acid, crystals (powd.).....	Lb.	7	@	7 1/2
Brimstone (crude, domestic).....	Ton	22.00	@	22.50
Bromine, bulk.....	Lb.	30	@	35
Calcium Chloride, fused.....	C.	60	@	90
Chalk (light precipitated).....	Lb.	4	@	4 1/2
China Clay (imported).....	Ton	nominal		
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, powdered, Foreign.....	Ton	16.00	@	17.00
Green Vitriol (bulk).....	C.	55	@	60
Hydrochloric Acid (18°).....	C.	1.15	@	1.55
Iodine (resublimed).....	Lb.	3.55	@	3.60
Lead Nitrate.....	Lb.	8 1/8	@	8 1/4
Litharge (American).....	Lb.	6 1/4	@	6 1/2
Lithium Carbonate.....	Lb.	65	@	70
Magnesium Carbonate.....	Lb.	21	@	35
Magnesite "Calcined".....	Ton	28.50	@	29.50
Nitric Acid, 36°.....	Lb.	37 1/8	@	41 1/4
Phosphoric Acid (sp. gr. 1.75).....	Lb.	21 1/2	@	25 1/2
Phosphorus.....	Lb.	45	@	1.00
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, 50°.....	Lb.	6 1/4	@	7
Potassium Bromide.....	Lb.	39	@	40
Potassium Carbonate (calcined), 80 @ 85%.....	C.	3.25	@	3.30
Potassium Chlorate, crystals.....	Lb.	7 1/4	@	7 1/2
Potassium Cyanide (bulk), 98-99%.....	Lb.	19	@	24
Potassium Hydroxide.....	C.	4.00	@	4.25
Potassium Iodide (bulk).....	Lb.	2.95	@	3.00
Potassium Nitrate (crude).....	Lb.	4 1/2	@	5
Potassium Permanganate (bulk).....	Lb.	9 3/4	@	10
Quicksilver, Flask (75 lbs.).....	Lb.	38.00	@	40.00
Red Lead (American).....	Lb.	6 1/2	@	6 1/4
Salt Cake (glass-makers').....	C.	55	@	65

Silver Nitrate.....	Oz.	37 1/2	@	38
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash (48 per cent).....	C.	67 1/2	@	72 1/2
Sodium Acetate.....	Lb.	3 1/4	@	4 1/8
Sodium Bicarbonate (domestic).....	C.	1.00	@	1.10
Sodium Bicarbonate (English).....	Lb.	2 1/4	@	3
Sodium Bichromate.....	Lb.	4 1/8	@	5 1/8
Sodium Carbonate (dry).....	C.	60	@	80
Sodium Chlorate.....	Lb.	7 1/4	@	7 1/2
Sodium Hydroxide, 60 per cent.....	C.	1.55	@	1.57 1/2
Sodium Hyposulfite.....	C.	1.30	@	1.60
Sodium Nitrate, 95 per cent, spot.....	C.	2.25	@	2.30
Sodium Silicate (liquid).....	C.	65	@	1.50
Strontium Nitrate.....	Lb.	67 1/8	@	7 1/8
Sulfur, Flowers (sublimed).....	C.	2.20	@	2.60
Sulfur, Roll.....	C.	1.85	@	2.15
Sulfuric Acid, 60° B.....	C.	85	@	1.00
Talc (American).....	Ton	15.00	@	20.00
Terra Alba (American), No. 1.....	C.	75	@	80
Tin Bichloride (50°).....	Lb.	12 1/2	@	13 1/2
Tin Oxide.....	Lb.	45	@	45 1/2
White Lead (American, dry).....	Lb.	5 1/4	@	5 1/2
Zinc Carbonate.....	Lb.	9	@	10
Zinc Chloride (granulated).....	Lb.	4 1/2	@	5
Zinc Oxide (American process).....	Lb.	5 1/8	@	6 1/8
Zinc Sulfate.....	Lb.	2 1/2	@	3

OILS, WAXES, ETC.

Beeswax (pure white).....	Lb.	42	@	45
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil (No. 3).....	Lb.	87 1/2	@	10
Ceresin (yellow).....	Lb.	12	@	22
Corn Oil.....	C.	6.60	@	6.65
Cottonseed Oil (crude), f. o. b. mill.....	Gal.	45	@	45 1/2
Cottonseed Oil (p. s. y.).....	Lb.	7 1/8	@	7 1/4
Cylinder Oil (light, filtered).....	Gal.	21 1/2	@	32
Japan Wax.....	Lb.	9 1/8	@	9 1/4
Lard Oil (prime winter).....	Gal.	92	@	94
Linseed Oil (raw).....	Gal.	46	@	47
Menhaden Oil (crude).....	Gal.	35	@	—
Neatsfoot Oil (20°).....	Gal.	96	@	98
Paraffine (crude, 120 & 122 m. p.).....	Lb.	3 1/2	@	3 1/4
Paraffine Oil (high viscosity).....	Gal.	26	@	28
Rosin ("F" grade) (280 lbs.).....	Bbl.	4.20	@	4.35
Rosin Oil (first run).....	Gal.	27	@	28
Shellac, T. N.....	Lb.	21	@	22
Spermaceti (cake).....	Lb.	30	@	35
Sperm Oil (bleached winter), 38°.....	Gal.	72	@	74
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid (double-pressed).....	Lb.	9	@	12
Tallow (acidless).....	Gal.	62	@	63
Tar Oil (distilled).....	Gal.	30	@	31
Turpentine (spirits of).....	Gal.	47	@	47 1/2

METALS

Aluminum (No. 1 ingots).....	Lb.	19	@	19 1/2
Antimony (Hallet's).....	Lb.	7 1/4	@	7 1/2
Bismuth (New York).....	Lb.	2.05	@	2.10
Bronze powder.....	Lb.	50	@	3.00
Copper (electrolytic).....	Lb.	15 1/4	@	15 1/2
Copper (lake).....	Lb.	15 1/8	@	15 1/4
Lead, N. Y.....	Lb.	4.30	@	—
Nickel.....	Lb.	50	@	55
Platinum (refined).....	Oz.	43.50	@	44.50
Silver.....	Oz.	59	@	60
Tin.....	C.	40.00	@	41.00
Zinc.....	C.	5.25	@	5.30

FERTILIZER MATERIALS

Ammonium Sulfate.....	C.	3.02 1/2	@	3.05
Blood, dried.....	Unit	3.30	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	27.25	@	28.00
Calcium Nitrate (Norwegian).....	C.	2.05	@	2.10
Castor meal.....	Unit	3.30	@	—
Fish Scrap, domestic, dried.....	Unit	nominal		
Mowrah meal.....	Ton	nominal		
Phosphate, acid, 16 per cent bulk.....	Ton	—	@	6.75
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium, "muriate," basis 80 per cent.....	Ton	38.55	@	—
Pyrites, furnace size, imported.....	Unit	0.13 1/4	@	—
Tankage, high-grade.....	Unit	3.25	@	10

AUTHOR INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY VOLUME V, 1913

ABRAHAM, H. Classification of Bituminous and Resinous Substances.....	11
Natural Rock Asphalts and Bitumens, by Danby (Book Review).....	1032
ADAMS, M. AND A. HOLMES. Pine Nut Oil.....	285
AGETON, C. N. AND P. L. GILE. Lime-Magnesia Ratio in Soil Analyses.....	33, 564
ALLEN, I. C. AND A. S. CROSSFIELD. U. S. Bureau of Mines Flash Point Testers.....	908
ALSBERG, C. L. Biochemistry. Chairman's Address at 48th Meeting A. C. S., Rochester.....	1019
ASTON, J. AND C. F. BURGESS. Influence of Various Elements on Corrosion of Iron.....	458
AXTELL, F. C. Sakai Celluloid Co. Plant in Japan.....	38
AYRES, W. S. Technical Problems of Coal Preparation.....	68
BAEKELAND, L. H. Chemical Constitution of Resinous Phenolic Condensation Products. Address of Acceptance. Willard Gibbs Medal Award.....	506
Investigation of U. S. Patent Office.....	417
Protection of Intellectual Property.....	51
U. S. Patent Office Index to Chemical Literature (Ed.).....	534
BAILEY, E. G. Coal, and the Prevention of Explosions and Fires in Mines, by Harger (Book Review).....	707
Coal, its Composition, Analysis, Utilization and Valuation, by Sommermeier (Book Review).....	620
BAILEY, E. H. S. AND G. O. PETERSON. Hickory Nuts and Their Oil.....	739
BAILEY, L. H. Improved Gooch Crucible Holder.....	756
BANCROFT, W. D. AND T. R. BRIGGS. Blue Gelatine Copper.....	9
BARDWELL, C., B. A. BERRYMAN, T. B. BRIGHTON AND K. D. KUHR. Hydrocarbons of Utah.....	973
BARKER, P. Heat Distribution in Operation of Steam Boilers.....	670
Sulfur in Coal. Preliminary Report by Am. Soc. T. M. and A. C. S. Committee.....	524
BARNES, G. W. Use of Natural Gas in Steam Boilers.....	486
BARTOW, E. Treating Turbid Waters with Calcium Hypochlorite.....	18
BASKERVILLE, C. American Oil Shales.....	73
AND H. S. RIEDERER. Chlorine Substitution Products of Methane from Natural Gas.....	5
AND W. A. HAMOR. Chemistry of Anaesthetics, V: Ethyl Chloride.....	828
BECKER, J. AND L. B. ROBERTSON. Production and Industrial Application of By-product Coke Oven Gases.....	491
BELDEN, A. W. Beehive Coke Oven Industry of the U. S.....	71
BENNER, R. C. AND J. J. O'CONNOR, JR. The Smoke Nuisance.....	587
BENSON, H. K. Laboratory Column Still.....	1018
AND M. DARRIN. Experimental Wood Distillation Plant.....	935
BEROLZHEIMER, D. D. New Publications.....	87, 175, 263, 352, 439, 529, 622, 708, 788, 877, 962, 1033
Science of Hygiene, by Pakes (Book Review).....	262
BERRY, F. AND L. H. VAN BUSKIRK. Modified Bank of Ammonia Stills.....	941
BERRYMAN, B. A., C. BARDWELL, T. B. BRIGHTON AND K. D. KUHR. Hydrocarbons of Utah.....	973
BILLINGS, H. E. AND A. SMITH. Fertilization of Citrus Soils.....	415
BIRCHBY, J. A. AND E. S. MERRIAM. Testing Natural Gas for Gasoline Production.....	824
BIRD, M. Interesting Soil Water Question in British Guiana.....	1012
BISHOP, E. S. AND W. D. BONNER. Rate of Reaction of Nitrous Acid and Urea in Dilute Solutions.....	134
BIZZELL, J. A. AND T. L. LYON. Influence of Preceding Crop on Nitrication in Soil.....	136
Lime Requirement of Soils.....	1011
BJERREGAARD, A. P. Apparatus for Determining Melting Points of Substances of Indefinite Melting Point.....	938
BLENNINGER, A. V. Natural History of Clay, by Searle (Book Review).....	707
Refractories and Furnaces, by F. T. Havad (Book Review).....	262
Transactions of the American Ceramic Society, Vol. XIV (Book Review).....	260
BOGERT, M. T. The Chemical Industries and the Universities.....	757
BONNER, W. D. AND E. S. BISHOP. Rate of Reaction of Nitrous Acid and Urea in Dilute Solutions.....	134
BOOTH, W. M. The Chemical Engineer and Industrial Efficiency.....	237
Water Supply for the Manufacturer.....	604
BORN, S. What's the Matter with the American Chemist? Note.....	785
BOSWORTH, A. W. AND O. FOLIN. Application of Folin's Method for the Determination of Ammonia to Fertilizers.....	485
BOUGHTON, E. W. Effect of Pigments on Linseed Oil, and Manganese Content of Raw Linseed Oil.....	282
BRACKETT, R. N. Decrease of Available Phosphoric Acid in Mixed Fertilizers Containing Acid Phosphate and Calcium Cyanamid.....	933
BRADY, W. Methods of Iron and Steel Analyses Used in American Rolling Mill Co. Laboratories (Book Review).....	620
BRAGO, C. T. American Alcohol Insoluble Test for Shellac.....	435
BRECKENRIDGE, J. E. Committee on Potash. Fertilizer Division, A. C. S., 47th Meeting, Milwaukee.....	431
Division of Fertilizer Chemistry, A. C. S., Milwaukee Meeting.....	431
Fertilizer Chemistry. Division Report, 48th Meeting A. C. S., Rochester.....	956
BRIGGS, C. H. Pure Food and Drug Law Alcohol Requirement and Assay.....	29
BRIGGS, T. R. AND W. D. BANCROFT. Blue Gelatine Copper.....	9
BRIGHTON, T. B., B. A. BERRYMAN, C. BARDWELL AND K. D. KUHR. Hydrocarbons of Utah.....	973
BROCK, F. P., L. V. REDMAN AND A. J. WEITH. Bromination of Phenol for Quantitative Determinations.....	389
Drying Rates of Raw Paint Oils.....	630
Rapid Volumetric Method for Cresols, Thymol and Phenol.....	831
BROKAW, A. D. Precipitation of Gold by Manganous Salts.....	560
BROOKS, A. W. AND C. A. PETERS. Microorganisms in Commercial Lime-Sulfur.....	1013
BRYAN, A. H. Use of Light Filter Cell in Polarizing High Grade Sugars.....	167
BRYSON, L. T. Electric Heater for Laboratory Distillations.....	49
BUCK, D. M. Copper in Steel—Influence on Corrosion.....	447
BUCKMINSTER, P. D. AND S. H. KATZ. Calcium Thioarsenate Spray.....	663
BUNDY, L. A. AND H. V. TARTAR. Soluble Arsenic in Lead Arsenate and Soap Mixtures.....	561
BURGESS, C. F. AND J. ASTON. Influence of Various Elements on Corrosion of Iron.....	458
BURRELL, G. A. Methods of Gas Analysis (German) by Hempel (Book Review).....	787
Notes on Mine Gas Problems.....	181
AND F. M. SEIBERT. Condensation of Gasoline from Natural Gas.....	895
BUSWELL, A. M. Ozone (Ed.).....	882
CAIN, J. R. AND F. H. TUCKER. Phosphorus in Steels Containing Vanadium.....	647
CALBREATH, J. F. Needs of the Mining Industry.....	236
CAMERON, F. K. Calcium Cyanamid, by Pranke (Book Review).....	961
CAMP, J. M. Note on New Form of Orsat Apparatus.....	84
CAMPBELL, E. D. Constitution of Portland Cement Clinker.....	627
Convenient Device for Analytical Ignitions.....	675
CAMPBELL, W. Iron and Steel by Hudson and Bengough (Book Review).....	874
CARPENTER, F. B. Fertilizer Legislation Committee Report. Fertilizer Division, 48th Meeting A. C. S., Rochester.....	957
Phosphate Rock Committee Report. Fertilizer Division, 48th Meeting A. C. S., Rochester.....	957
Soil Conditions and Plant Growth, by E. J. Russell (Book Review).....	86
Soil Fertility and Fertilizers, by J. E. Halligan (Book Review).....	174
Standard Sample of Phosphate Rock. Fertilizer Division, A. C. S.....	344
CATHCART, W. R. AND F. J. FALDING. High Form of Sulfuric Acid Chamber.....	223
CHAMBERLAIN, G. D. Developments of Iron and Steel Industry (Ed.).....	357
CHANDLER, C. F. Presentation Address. Perkin Medal Award.....	241
CHURCH, S. R. Testing Tars, Oils and Pitches.....	195
CLEMENT, J. K. AND L. V. WALKER. Electrolytic Prevention of Iron and Steel Corrosion.....	361
COMEY, A. M. Explosives, by Brunswig, Munroe-Kebler (Translation) (Book Review).....	1032
CONNER, A. B. Sulfur in Pyrites Cinders.....	399
COOK, F. C. Analyses of Bouillon Cubes.....	989
COWLES, A. H. Alumina and Aluminum from Mineral Silicates.....	331
CRAWFORD, S. L. Detection of Adulteration of Cider Vinegar with Distilled.....	845

CROSSLAND, A. S. AND I. C. ALLEN. U. S. Bureau of Mines. Flash Point Tester.....	908
CROWN, H. A. AND C. E. G. FORST. Polarimetric Method for Starch in Paper.....	304
CURRIS, C. C. U. S. Forestry Service. Investigations. (Ed.).....	676
CUSHMAN, A. S. Electric Furnace in Iron and Steel Oxygen Determinations. A Criticism.....	349
AND E. B. WEDENBERG. Electrolytic Method for Tin in Canned Foods.....	347
DARRIN, M. AND H. K. BENSON. Experimental Wood Distillation Plant.....	935
DAVIDSON, D. Metallic Pigments.....	83
DAYOLL, D. L., JR. Technical and Chemical Control in Sugar Manufacture.....	313
DEAN, A. L. AND C. R. DOWNS. Antiseptic Tests of Wood Preserving Oils.....	126
DECHUER, J. A. Disinfection and Disinfectants, by Christian (Book Review).....	876
DEMAREST, D. J. Analysis of Alloys of Lead, Tin, Antimony and Copper.....	842
Chromium and Vanadium in Steel. A Correction.....	84
Determination of Zinc in Ores.....	302
Electrolytic Method for Copper in Ores Containing Arsenic, Antimony or Bismuth.....	216
Sulfoeyanate Permanganate Method for Copper in Ores.....	215
DEWEY, P. P. Gay-Lussac Method of Silver Determination.....	209
DICKINSON, H. C. Calorific Power of Coal. Preliminary Report by Am. Soc. T. M. and A. C. S. Committee.....	525
DOLE, R. B. Composition of Salines, Silver Peak Marsh, Nev.....	196
DOWNS, C. R. AND A. L. DEAN. Antiseptic Tests of Wood Preserving Oils.....	126
DUBOIS, N. A. Protection of Steel and Iron by Paint Films.....	968
DURAND, H. Determination of Saccharin in Foods.....	987
DUTCHER, R. A. Determination of Lime in Cow Feces.....	37
Correction.....	260
EARLE, R. B. AND A. H. FISKE. Destructive Distillation of Sewage Sludge.....	186
ELLIOT, A. H. American Gas Institute Proceedings, 6th Annual Meeting, St. Louis (Book Review).....	437
ELLIS, C. Chemistry of the Oil Industries, by Southcombe (Book Review).....	1031
Hydrogenation of Oils.....	95
ELLMS, J. W. AND S. J. HAUSER. Ortho-Tolidine as Reagent for Colorimetric Estimation of Small Quantities of Free Chlorine.....	915
Correction.....	1030
ERICSON, E. J. Technical Method of Spelter Analysis.....	401
FALDING, F. J. AND W. R. CATHCART. High Form of Sulfuric Acid Chamber.....	223
FARAGHER, W. F. A Standard Viscosimeter and Standard Methods for Determining Viscosities—Why Not? A Note.....	167
FARNHAM, G. Phosphoric Acid Committee Report. Fertilizer Division, 48th Meeting A. C. S., Rochester.....	956
FIELDNER, A. C. Accuracy and Limitations of Coal Analysis.....	270
Preparation of Laboratory Samples of Coal. Preliminary Report by Am. Soc. T. M. and A. C. S. Committee.....	518
FINK, C. G. Applications of Ductile Tungsten.....	8
FINKBINER, N. M. AND W. VAN WINKLE. Water of Crater Lake, Ore.....	198
FISKE, A. H. AND R. B. EARLE. Destructive Distillation of Sewage Sludge.....	186
FOLIN, O. AND A. W. BOSWORTH. Application of Folin's Method for the Determination of Ammonia to Fertilizers.....	485
FORBES, E. B. AND J. E. MENSCHING. Improved Crude Fiber Estimation.....	258
FOX, C. P. Adapted Wiley Extractor for Rubber.....	417
Improved Laboratory Burner.....	1019
Syrian Autoburning Limestone.....	1029
Wild Lettuce Rubber.....	477
FOX, P. J. Titration of Calcium and Magnesium in Same Solution.....	910
FRANKLIN, F. H. Fusion Method for Sulfur in Iron and Steel.....	839
FRAPS, G. S. Effect of Ignition on Solubility of Soil Phosphates.....	416
FRARY, F. C. AND M. G. MASTIN. Zinc in Treated Ties.....	738
FRY, W. H. Analysis of Soils, Mineralogical.....	30
Condition of Soil Phosphoric Acid Insoluble in Hydrochloric Acid.....	664
AND J. G. SMITH. Composition of Sediments from Potomac and Shenandoah Rivers.....	1009
GAINES, R. H. Corrosion of Lead.....	766
GAITHER, E. W. Comparison of Some Qualitative and Quantitative Methods for Carbonates in Soils.....	138
GARRATT, F. Colorimetric Method for Chromium in Steel.....	298
GAYLEY, J. Address of Acceptance. Perkin Medal Award.....	241
GEHART, F. C. Hydraulic for Use in Nitrogen Work, Etc.....	490
GILL, P. L. AND C. N. AGEFON. Lime-Magnesia Ratio in Soil Analyses.....	33, 564
GILLET, H. W. The Chemist and Scientific Management.....	593
GOODSON, E. H. AND L. M. TOLMAN. Cider Vinegars Made by Generator Process.....	928
GORENBER, R. A. AND A. J. HARRIS. Relation between Weight of Sugar Beet and Composition of Its Juice.....	192
GRIFFIN, M. L. Government's Interests in the Pulp and Paper Industry.....	500
Note on Rosh in Paper.....	960
GROSS, D. M. "What's the Matter with the American Chemist?".....	692
GROSSKOPF, W. M. Relation of Manufacturer to Our Patent System.....	685
Some Peculiar Functions of the Retained Expert.....	772
GUDEMANN, E. Analyses of Confectioners' Glucose.....	665
HABER, F. AND R. LE ROSSIGNOL. Synthetic Ammonia.....	328
HALE, P. E. AND T. W. MIELKE. Winkler's Method for Oxygen in Water, Effect of Nitrite and its Prevention.....	976
HALVERSON, J. O. Comparison of Modified Babcock and Rose-Gottlieb Methods for Fat in Ice Cream.....	480
Modified Babcock for Fat in Ice Cream.....	403
Sampling Ice Cream.....	409
HAMOR, W. A. Chemical Industries of Belgium, Netherlands, Norway and Sweden, by Norton (Book Review).....	528
Control of Public Utilities (Ed.).....	967
Current Industrial News.....	74, 161, 251, 337, 423, 511, 605, 695, 774, 861, 950, 1024
New and Non-Official Remedies, 1911, by American Med. Assoc. Press (Book Review).....	707
Obituary—F. H. Daniels.....	871
Obituary—Jules Ogier.....	1030
Present Status of Window Glass Industry.....	80
Utilization of Atmospheric Nitrogen, by T. H. Norton (Book Review).....	437
AND C. BASKERVILLE. Chemistry of Anaesthetics, V: Ethyl Chloride.....	828
HANDY, J. O. Copper Covered Steel.....	884
HARDER, O. E. Note on Standard Vanillin Solution for Folin Colorimetric Determination of Vanillin.....	619
HARDING, E. P. AND E. JOHNSON. Hydrogen Sulfide in Illuminating Gas.....	836
AND G. PARKIN. Milk-Fat in Evaporated Milk and Milk Powders.....	131
Fat in Ice Creams, Cereals and Chocolate.....	843
HARE, C. L. Effects of Feeds on Lards, II.....	410
HARRIS, J. A. AND R. A. GORTNER. Relation between Weight of Sugar Beet and Composition of Its Juice.....	192
HART, E. Dr. Gayley's Interest in Education. Address. Perkin Medal Award.....	247
HARTZELL, J. C. What's the Matter with the American Chemist? Note.....	871
HAUSER, S. J. AND J. W. ELLMS. Ortho-Tolidine as Reagent for Colorimetric Estimation of Small Amounts of Free Chlorine.....	915
Correction.....	1030
HAWLEY, L. F. Efficiency Studies in Hardwood Distillation.....	445
HAYNES, E. Alloys of Cobalt with Chromium, Etc.....	189
HEALY, L. J. D. Electric Desiccator for Analysis of India Rubber and Other Organic Compounds.....	489
HÉROULT, P. L. V. Recent Developments in Electric Steel Furnace.....	47
HERTY, C. H. Naval Stores Industry.....	65
HESSE, B. C. Cooperation among Chemists and Manufacturers.....	92
Patent Expert and Chemical Manufacturer.....	854
Problem of International Congresses of Applied Chemistry.....	321
Secretary's Report of 8th International Congress of Applied Chemistry.....	344
Suggestions as to Programs of Sectional Meetings of the A. C. S.....	1020
HIBBARD, P. L. Study of Pemberton-Kilgore Determination of Phosphoric Acid.....	998
HICKS, W. B. Rapid Modified Chlorplatinate Method for Potassium.....	650
HILLEBRAND, W. F. Moisture in Coal. Preliminary Report by Am. Soc. T. M. and A. C. S. Committee.....	521
HINMAN, J. J., JR. Total Formaldehyde in Fumigators and Commercial Solutions.....	752
HOFFMAN, C. AND W. E. TOTTINGHAM. Action of Fermenting Manure on Reinforcing Phosphates.....	199
HOLMES, A. AND M. ADAMS. Pine Nut Oil.....	285
HORNE, W. D. Handbook of Sugar Analysis, by Browne (Book Review).....	172
World's Cane Sugar Industry, by Geerligs (Book Review).....	85
HOTTEL, H. C. Sterilization of Water Supply at Trenton.....	319
HOWE, H. E. Some Projection Experiments with Spectra.....	578
HOWE, H. M. The Value of Expert Opinions. Address. Perkin Medal Award.....	246

HUBBARD, P. AND C. S. REEVE. Effect of Exposure on Bitumens... Correction.....	15 260
HULBERT, E. C. Improved Apparatus for Testing Jelly-Strength of Gluces.....	235
JACKMAN, W. F. Obituary—Alfred Bellamy Aubert.....	171
JACKSON, D. D. Water, its Purification and Use in the Industries, by Christie (Book Review).....	351
JAMES, J. H. Acetylene Solvents..... Textbook of Chemical Technology and Metallurgy, edited by Newmann (Book Review).....	115 173
JAMIESON, GEO. S. Phosphates in Surface Waters.....	301
JESSE, R. H., JR. Gases Formed in Anaerobic Sewage Decomposi- tion.....	636
JOHNSON, C. M. Oxygen in Tungsten Powder and Steel..... Phosphorus in Ferro-tungsten, Tungsten Powder and Oxide and Tungstic Acid by Direct Solution.....	295 297
Tapered Clay Inlet and Outlet to Eliminate Rubber Stoppers from Vitrifired Clay Combustion Tube.....	581
Vitrified Clay Combustion Tube with Tapered Outlet for the Determination of Carbon in Steels, Ferro Alloys and Graphite..	488
JOHNSON, E. AND E. P. HARDING. Hydrogen Sulfide in Illuminating Gas.....	836
JOYCE, C. M. AND H. LA TOURETTE. Nitrogen Determined by the Nitrometer.....	1017
KAHLENBERG, L. Obituary—W. W. Daniells.....	80
KATZ, S. H. AND P. D. BUCKMINSTER. Calcium Thioarsenate Spray KEBLER, L. F. Tincture of Iodine.....	663 484
KITA, G. Some Properties of Koji Diastase.....	220
KRESS, O. Chloride of Lime in Sanitation, by Hooker (Book Re- view).....	350
Materials Used in Sizing, by Ermen (Book Review).....	787
KUHRE, K. D., C. BARDWELL, B. A. BERRYMAN AND T. B. BRIGHTON. Hydrocarbons of Utah.....	973
KUNBERGER, A. F. Efficiency of Oxides for Gas Purification.....	580
KUNZ, G. F. Prof. Paul Walden. Biographical Sketch with Bibli- ography.....	611
LANGMUIR, A. C. Note on Analysis of Crude Glycerine.....	871
LA TOURETTE, H. AND C. M. JOYCE. Nitrogen Determined by the Nitrometer.....	1017
LATSHAW, W. L. AND P. RUDNICK. Neutral Ammonium Citrate.....	998
LAW, L. M. Empirical Requirements in Asphalt Specifications. Address.....	1021
LE ROSSIGNOL, R. AND F. HABER. Synthetic Ammonia.....	328
LEVIN, I. H. Synthesis of Precious Stones.....	495
LEWIS, R. H. AND C. S. REEVE. Dimethyl Sulfate Test for Small Amounts of Petroleum or Asphalt Products in Tars.....	293
LICHTENBERG, H. F. Rapid Method for Fat in Ice Cream.....	786
LIEBER, H. Gas and Oil Combustion Co. Formed. Note.....	84
LINDEMUTH, J. R. AND A. R. MERZ. Leaching Potash from Freshly Cut Kelp.....	729
AND E. G. PARKER. Analyses of Fish Scrap..... Analyses of Pacific Coast Kelps.....	388 287
LIPMAN, C. B. AND H. F. PRESSEY. Nitrogen in Humus Determina- tions.....	143
LITTLE, A. D. Industrial Research in America. Presidential Ad- dress, 48th Meeting A. C. S., Rochester.....	793
LOEW, O. Influence of Lime-Magnesia Ratio upon Plant Growth. Note.....	959
LOHR, J. M. Metallic Alloys, by Gulliver (Book Review).....	874
LONG, E. W. AND C. E. MAY. Properties of Watered Milk.....	573
LUCAS, H. J. Determination of Nitrobenzol in Peanut Oil.....	576
LUCKE, C. E. Comparative Fuel Values of Gasoline and Denatured Alcohol in Internal Combustion Engines, by Stroug and Stone (Book Review).....	173
Design of Surface Combustion Appliances..... Correction.....	801 960
LYON, T. L. AND J. A. BIZZELL. Influence of Preceding Crop on Nitrification in Soil.....	136
Lime Requirement of Soils.....	1011
LYTHGOE, H. C. Massachusetts Milk Supply Inspection by State Board of Health.....	922
MABERY, C. F. Lubrication with Oils and with Colloidal Graphite MACNIDER, G. M. Modified Extraction Apparatus.....	717 150
MAHR, H. W. Melting Point of Greases by Means of N. Y. Testing Laboratory Viscosimeter.....	674
MANNHARDT, H. Oxygen Absorption Test for Linseed Oil.....	129
MARRS, L. E. American Fertilizer Handbook, 1913 (Book Review) General Index to Chemical News, Vols. 1 to 100 (Book Review) AND F. J. METZGER. Volumetric Determination of Manganese in Rock, Slags, Ores and Spiegels.....	961 961 125
MARTI, W. C. AND A. J. PATTEN. Neutral Ammonium Citrate Solu- tion.....	567
MASON, G. F. Agricultural and Food Chemistry Division Report. 48th Meeting A. C. S., Rochester.....	956
MASTIN, M. G. AND F. C. FRARY. Zinc in Treated Ties.....	738
MATHEWSON, W. E. Separation of Mixtures of Acid Coal Tar Dyes MATOS, I. J. General Efficiency in Dyehouses and Bleach Works.....	26 693
MATTHEWS, J. M. The Hydrosulfite (German), by Jellinek (Book Review).....	174
What's the Matter with the American Chemist? (Ed.).....	626
MAY, C. E. AND E. W. LONG. Properties of Watered Milk.....	573
MCBRIDE, R. S. AND E. R. WEAVER. Sulfur in Illuminating Gas... Sulfate in Ammonium Sulfate Solution. Testing Illuminating Gas.....	474 469
Correction.....	619
MCCABE, C. R. Titanium in Iron and Steel.....	735
Note.....	872
Vanadium in Steel by the Hydrogen Peroxide Color Method....	736
MCCARTHEY, W. J. Mineralogical Soil Analysis.....	562
MCCHARLES, C. H. An Automatic Pipette.....	735
MCILHINEY, P. C. Analysis of Paint and Varnish Products, by Holley (Book Review).....	174
McMILLAN, R. H. Electric Resistance Furnace for Oxygen in Iron and Steel.....	123
McMURTRIE, D. C. Bibliography of Scientific Writings by William McMurtrie.....	617
McMURTRIE, W. Disposal of Sewage with Recovery of Elements of Plant Food for Use in Agriculture.....	156
MEADE, R. K. Action of Various Substances on Concrete..... Depreciation and Obsolescence. Address.....	723 762
Manual of Cement Testing, by Richards and North (Book Re- view).....	707
MEADER, J. W. AND F. A. MILLER. Assay of Individual Plants of Various Species of <i>Datura</i> , Etc.....	1014
MELIA, T. W. AND F. E. HALB. Winkler's Method for Oxygen in Water; Effect of Nitrite and its Prevention.....	976
MENSCHING, J. E. AND E. B. FORBES. Improved Crude Fiber Esti- mation.....	258
MERRIAM, E. S. AND J. A. BIRCHBY. Testing Natural Gas for Gas- oline Production.....	824
MERZ, A. R. AND J. R. LINDEMUTH. Leaching Potash from Freshly Cut Kelp.....	729
METZGER, F. J. AND L. E. MARRS. Volumetric Determination of Manganese in Rock, Slags, Ores and Spiegels.....	125
MILFORD, L. R. Recent Analyses of Saratoga Mineral Waters, II, III.....	24 557
MILLAR, C. E. Parr Total Carbon Apparatus Modified.....	234
MILLER, F. A. AND J. W. MEADER. Assay of Individual Plants of Various Species of <i>Datura</i> , Etc.....	1014
MITCHELL, L. C. AND L. M. TOLMAN. Composition of Different Varieties of Red Peppers.....	747
MUCKENFUS, A. M. Practical Accelerated Test for Paints and Varnishes.....	535
MUNROE, C. E. Centenary of Gas Industry. A. C. S. Committee Report.....	81
MURPHY, R. K. Chemical Works, their Design, Erection and Equip- ment, by Dyson and Clarkson (Book Review).....	786
Henley's 20th Century Book of Recipes, Formulas and Processes (Book Review).....	86
AND M. C. WHITAKER. Chemical Engineering and the New Laboratories at Columbia University.....	304
MURRAY, B. L. Determination of Small Amounts of Caffeine.....	668
NELSON, J. M. Allen's Commercial Organic Analysis, VII (Book Review).....	1032
NOWAK, C. A. Influence of Ozone on Yeast and Bacteria..... Training of the Fermentologist.....	668 502
NOYES, W. A. Preliminary Report for the Committee on Coal Analysis of the Am. Soc. for Testing Materials and the A. C. S.	517
O'CONNOR, J. J., JR. AND R. C. BENNER. Smoke Nuisance....	587
O'LOUGHLIN, C. C. Mineral Aggregate in Bitumen Pavements.....	320
OLSON, G. A. Quantitative Estimation of Gliadin in Flour and Gluten.....	917
PARKER, C. L. Recent Inventions.....88, 176, 264, 353, 440, 531, 623, 709, 789, 878, 963, 1034	388
PARKER, E. G. AND J. R. LINDEMUTH. Analyses of Fish Scrap.....	287
Analyses of Pacific Coast Kelps.....	432
PARKER, T. J. Dr. Friedrich W. C. Schmiedewitz. Obituary.....	438
Treatise on General and Industrial Inorganic Chemistry, by Mohr (third edition) (Book Review).....	438
PARKIN, G. AND E. P. HARDING..... Milk Fat in Evaporated Milk and Milk Powders.....	131
Fat in Ice Creams, Cereals and Chocolate.....	843

PARK, S. W. Ash in Coal. Preliminary Report by Am. Soc. T. M. and A. C. S. Committee	583	SEBERT, F. M. AND G. A. BUDDELL. Condensation of Gasoline from Natural Gas	895
Volatile Matter in Coal. Preliminary Report by Am. Soc. T. M. and A. C. S. Committee	582	SIEDENBERG, A. Detection of Gelatin in Sour Cream	927
PARKSONS, C. L. American Chemical Society. Rochester Meeting. Announcement	701	SIEMI, L. Report of Another Platinum Robbery	528
Our Radium Resources. Address	943	SHARPLES, P. P. Distillation of Tar	466
Uranium and Radium Situation (Ed.)	356	SHEPHERD, H. C. Fatty Foods, Their Practical Examination, by Bolton and Revis (Book Review)	787
PATTER, A. J. AND W. C. MARSH. Neutral Ammonium Citrate Solution	567	Industrial and Manufacturing Chemistry, by Martin (Book Review)	1030
PATTERSON, A. M. On Criticism of Chemical Abstracts	783	SHERWOOD, N. P. AND C. C. YOUNG. Deterioration of Soda Water Due to Microorganisms	577
PERKINS, G. B. Liquid Air—Oxygen—Nitrogen, by Claude (Book Review)	876	SHINOSAKI, Y. On Japanese Peppermint Oil	658
Correction	1033	Peppermint Oil Industry in Japan	656
PINCE, C. M. Potassium Permanganate in the Quantitative Estimation of Some Organic Compounds	218	SIDENER, C. E. AND P. M. SKARTVEDT. Method for Phosphorus in Vanadium Steel and Ferrovanadium	838
PERKIN, W. H. Permanent Fireproofing of Cotton Goods	57	SKARTVEDT, P. M. AND C. F. SIDENER. Method for Phosphorus in Vanadium Steel and Ferrovanadium	838
PERKINS, A. E. New Form of Laboratory Extraction Apparatus	148	SMALLEY, F. N. Total Fatty Acids in Cottonseed Fats	402
PERRY, R. P. Tar Distillation in the U. S.	151	SMITH, A. Service Chemistry, by Lewis and Brame (Book Review)	875
PETERS, C. A. AND A. W. BROOKS. Microorganisms in Commercial Lime Sulfur	1013	SMITH, A. AND H. E. BILLINGS. Fertilization of Citrus Soils	415
PETERSON, G. O. AND E. H. S. BAILEY. Hickory Nuts and Their Oil	739	SMITH, H. E. Gas Bubble and Washing Tube for Combustion Apparatus	150
PILKINGTON, B. AND H. V. TARTAR. Comparative Study of Composition of Hops Grown in Different Parts of the World	478	SMITH, H. G. Precipitation of Barium Sulfate	416
PORTSCHKE, P. Determination of Sodium Borate in Soap	645	SMITH, J. G. Sponges as a Fertilizer	850
Sulfur Dioxide in Gelatin	980	AND W. H. FRY. Composition of Sediments from Potomac and Shenandoah Rivers	1009
FORST, C. E. G. AND H. A. CROWN. Polarimetric Method for Starch in Paper	304	SMITH, N. Valve for Desiccator	235
PORTER, H. C. AND G. B. TAYLOR. Specific Heat of Coal and its Relation to Combined Water	289	SMITH, O. C. Modification of Official Determination of Humus	35
PRANKE, E. J. Manufacture and Uses of Cyanamid	159	SNELL, J. F. The Analysis of Maple Products, I. An Electrical Conductivity Test for Purity of Maple Syrup	740
PRESSEY, H. F. AND C. B. LIPMAN. Nitrogen in Humus Determinations	143	AND J. M. SCOTT. Analysis of Maple Products, II. Comparative Study of Delicacy of Methods	993
RATHER, J. B. Humus in Hawaiian Soils by the Ammonium Carbonate Method	222	SOPER, G. A. Utilization of Sewage. Address	860
RAY, E. A. On Methods of Analysis of Crude Glycerin	784	SQUIBB, E. R. AND SONS. Combination Apparatus Stand	490
RAYMOND, R. W. The New Age. Address. Perkin Medal Award	249	STEWART, J. Plasticity of Clay	421
REDMAN, L. V., A. J. WEITH AND F. P. BROCK. Bromination of Phenol for Quantitative Determinations	389	STIEGLITZ, J. Chairman's Address. Willard Gibbs Medal Award	504
Drying Rates of Raw Paint Oils	630	STONE, G. C. Preparation and Uses of White Zinc Paints, by Fleury (Book Review)	261
Rapid Volumetric Method for Cresols, Thymol and Phenol	831	STRONG, W. W. Theory of Removal of Suspended Matter from Gases	858
REEVE, C. S. AND P. HUBBARD. Effect of Exposure on Bitumens	15	STUART, A. T. Corrosion of Metals by Water	905
AND R. H. LEWIS. Dimethyl Sulfate Test for Small Amounts of Petroleum or Asphalt Products in Tars	293	SURFACE, H. E. List of U. S. Public Documents on Pulp and Paper	614
REMYINGTON, J. P. 9th Revision U. S. Pharmacopoeia	429	TARTAR, H. V. AND B. PILKINGTON. Composition of Hops Grown in Different Parts of the World	478
RÉVERDIN, F. Analysis of Organic Dyestuffs. Sub-Commission. Note	259	AND L. A. BUNDY. Soluble Arsenic in Lead Arsenate and Soap Mixtures	561
RICHARDS, J. W. Serpek Process for Aluminum Nitride	335	TASSIN, W. Microstructure of Steel Castings	713
RICHARDSON, C. Native Bitumens and their Residuals	462	TAYLOR, F. O. Interpretation of U. S. P. Assay Processes	601
RICHARDSON, W. D. Presentation Address. Willard Gibbs Medal Award	505	TAYLOR, G. B. AND H. C. PORTER. Specific Heat of Coal and Its Relation to Combined Water	289
RIEDERER, H. S. AND C. BASKERVILLE. Chlorine Substitution Products of Methane from Natural Gas	5	TEEPLE, J. E. Utilizing Wood Waste. Address	680
RIGG, G. Deterioration of Firebricks during Service	549	THACHER, S. P. Arkosite	83
ROBERTSON, L. B. AND J. BECKER. By-Products Coke Oven Gases	491	THOMAS, A. W. Food Inspection and Analysis, by Leach (Book Review)	621
ROBISON, F. W. Food Standards and their Effect upon Food Law Enforcement	949	THOMAS, J. B. AND E. A. SANDMAN. Hypochlorite Disinfection of Baltimore City Water Supply	476
RONALD, J. T. Expert Testimony. Address	582	THOMPSON, A. R. Kukui (Candlenut) Oil	644
ROSS, W. H. Decomposition of Feldspar and its Use in the Fixation of Atmospheric Nitrogen	725	THOMPSON, G. W. Chemical Analysis of Lead and Its Compounds, by Schaeffer (Book Review)	351
RUDER, W. E. Intergranular Cement in Metals	452	Opacity and Hiding Power of Pigments. Tests	120
RUDNICK, P. Fertilizer Chemistry—A Report of Progress. Chairman's Address. 48th Meeting A. C. S., Rochester	948	THWING, C. B. Device for Controlling Small Electric Furnaces	149
AND W. L. LATSHAW. Neutral Ammonium Citrate	998	TOCH, M. Lead Poisoning. A Note	434
RUTH, W. E. The Lime Sulfur-Lead Arsenate Spray Mixture	847	Paint as an Engineering Material	366
Paints for Indicating the Uses of Pipes	784	TOLMAN, L. M. AND E. H. GOODNOW. Study of Cider Vinegars Made by Generator Process	928
SADTLER, S. P. Petroleum Analytical Methods	393	AND L. C. MITCHELL. Composition of Different Varieties of Red Peppers	747
SALISBURY, S. H., JR. Division of Industrial Chemists and Chemical Engineers, A. C. S., 47th Meeting, Milwaukee	430	TOTTINGHAM, W. E. AND C. HOFFMAN. Action of Fermenting Manure on Reinforcing Phosphates	199
Industrial Chemists and Chemical Engineers' Division Report. 48th Meeting A. C. S., Rochester	956	TRESCOT, T. C. Comparison of Kjeldahl-Gunning-Arnold with Official Kjeldahl and Official Gunning Methods for Nitrogen	914
New Descriptive Directory of Division of Industrial Chemists and Chemical Engineers of A. C. S. Note	616	TROY, H. C. Note on Calculating Fat-Free Residue of Milk	872
SAMMET, C. F. Quantitative Determination of Rosin in Paper	732	Note on Fat in Ice Cream	960
SANDMAN, E. A. AND J. B. THOMAS. Hypochlorite Disinfection of Baltimore City Water Supply	476	TUCKER, F. H. AND J. R. CAIN. Phosphorus in Vanadium Steels	647
SCHAEFFER, J. A. Chemical Laboratory of the Picher Lead Co.	850	TUCKER, S. A. Electro-Plating and Analysis of Solutions, by Reama (Book Review)	961
Manufacture and Properties of Sublimed White Lead	144	Electro-Plating, by Barclay and Hainsworth (Book Review)	620
SCHORGER, A. W. Oleoresins of Jeffrey and Singleleaf Pines	971	Principles of Applied Electrochemistry, by Allmand (Book Review)	529
SCHULTE, W. B. Influence of Cinders on Corrosion of Iron Imbedded in Clay	554	Production of Alumina and Fixation of Nitrogen	191
SCHWARZ, R. Use of Immersion Refractometer in Examining American Beers	660	TURRENTINE, J. W. Brines from the Ocean and Salt Lakes	19
SCOTT, J. M. AND J. F. SNELL. Analysis of Maple Products, II. Comparative Study of Delicacy of Methods	993	The Menhaden Industry	378
		TUTTLE, J. B. Sampling of Rubber Goods	618

TWINING, R. H. Accurate and Practical Viscosimeter.....	349	WEISS, H. F. Tests of Commercial Value of Wood Preservatives....	372
AND G. F. WHITE. Fluidity of Butter Fat and Its Substitutes...	568	WEISS, J. M. Coal Tar Light Oil in the U. S.	61
UTT, C. A. A. Analysis of Unsweetened Evaporated Milk.....	168	WEITH, A. J. I. V. REDMAN AND F. P. BROCK. Bromination of Phenol for Quantitative Determinations.	389
VAIL, J. G. Note on Producer Gas Analysis.....	756	Drying Rates of Raw Paint Oils.	630
VAN BUSKIRK, L. H. AND F. BERRY. Modified Bank of Ammonia Stills.....	941	Rapid Volumetric Method for Cresols, Thymol and Phenol ..	831
VAN HISE, C. R. Relation of Big Business to Industrial Prosperity with Special Reference to Mining. Address.....	946	WELD, F. C. Determination of "Volatile" in Coal.	169
VAN WINKLE, W. Water Analysis—Breitenbush Hot Springs, Ore...	300	Correction	260
AND N. M. FINKBINER. Water of Crater Lake, Ore.....	198	WELLS, S. D. Paper Pulp from Longleaf Pine by Soda and Sulfate Processes.....	906
VOORHEES, S. S. AND P. H. WALKER. Tests of Paints for Steel Ex- posed Alternately to Air and Fresh Water.....	899	WESSON, L. G. Direct Determination of Rubber.....	398
WAGGAMAN, W. W. A Possible Commercial Utilization of Nel- sonite.....	730	WETTENGEL, E. B. AND A. S. CUSHMAN. Electrolytic Method for Tin in Canned Foods.....	217
WAGNER, T. B. Efficiency in Chemical Industries—The Corn Pro- ducts Industry.....	677	WHIPPLE, D. Rubber Chemistry Section Report, 48th Meeting A. C. S., Rochester.....	956
WAHL, R. Some Distinctions between Pepsin and Peptase.....	752	WHITAKER, M. C. Dictionary of Applied Chemistry, by Thorpe. Vol. III (Book Review).....	620
WALKER, A. L. Hydro-Metallurgy of Copper, by Greenwalt (Book Review).....	86	AND R. K. MURPHY. Chemical Engineering and the New Labora- tories at Columbia University.....	304
WALKER, L. V. AND J. K. CLEMENT. Electrolytic Prevention of Cor- rosion of Iron and Steel.....	361	WHITE, G. F. AND R. H. TWINING. Fluidity of Butter Fat and Its Substitutes.....	568
WALKER, W. H. Corrosion of Iron and Steel.....	444	WHITE, H. L. Influence of Bran-Extracts on Baking Qualities of Flour.....	990
WALKER, P. H. AND S. S. VOORHEES. Tests of Paints for Steel Ex- posed to Air and Fresh Water Alternately.....	899	WHITNEY, W. R. Research Fund, Am. Electrochem. Soc. Note....	432
WARE, E. E. Control of Initial Setting of Portland Cement.....	369	WHITTELSEY, T. Synthesis of Rubber (German), by Ditmar (Book Review).....	174
WATERS, C. E. Evaporation Test for Mineral Lubricating and Transformer Oils.....	394	WILEY, H. W. William McMurtrie. Obituary.....	616
Gasoline Generator for Sulfur Determinations.....	853	WILEY, S. W. Reflux Condenser.....	151
WATKINS, W. H. What's the Matter with the American Chemist? Note.....	785	WILLIAMS, K. I. Chemical Composition of Cooked Vegetable Foods. Part III.....	653
WEAVER, E. R. AND R. S. MCBRIDE. Sulfate in Ammonium Sulfate Solution. Testing of Illuminating Gas.....	469	Correction	786
Correction.....	619	WITHEROW, J. R. Transactions of American Institute of Chemical Engineers, Vol. IV (Book Review).....	84
Sulfur in Illuminating Gas.....	474	WRIGHT, A. M. Chemistry in Relation to Frozen Meat Industry of New Zealand.....	673
WEBER, H. C. P. Modified Form of Stability Test for Explosives...	641	WYSOR, R. J. Letter Concerning Platinum Thief.....	259
WEINTRAUB, E. Boron: Properties and Preparation.....	106	Life of Platinum Crucibles Lengthened by Use of Méker Burner..	705
		YOUNG, C. C. AND N. P. SHERWOOD. Deterioration of Soda Water Due to Microorganisms.....	577

SUBJECT INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY VOLUME V, 1913

ABRASIVE, "Electric." Note.....	79	Ammonia in Fertilizers by Polin's Method. O. Polin and A. W. Bosworth.....	485
Abstracts, Chemical, On a Criticism of. A. M. Patterson.....	783	Ammonia Stills, Modified Bank of. F. Berry and L. H. Van Buskirk.....	941
Acetylene and Calcium Carbide, Industrial Uses of. Note.....	606	Ammonia, Synthetic. F. Haber and R. Le Rossignol.....	328
Acetylene Solvents. J. H. James.....	115	Ammonium Citrate Solution, Neutral, On Preparation of. P. Rudnick and W. I. Latshaw.....	998
Addresses. 51, 151, 236, 321, 417, 491, 582, 677, 757, 884, 943, 1019		Ammonium Citrate Solution, Neutral, Simple Preparation. A. J. Patten and W. C. Marti.....	567
Agricultural and Food Chemistry Division A. C. S. G. F. Mason, Secretary, 48th Meeting (Rochester) Report.....	956	Ammonium Sulfate in 1912. Note.....	253
Air Pumps, Condenser, Efficiency of. Note.....	516	Ammonium Sulfate, Use of, in China. Consular Note.....	171
Albamin and Lecithin Industry. Note.....	340	Anaesthetics, Chemistry of, V: Ethyl Chloride. C. Baskerville and W. A. Hamor.....	828
Alloys Production and Use in France. Note.....	1029	Annual Tables of Constants, Vol. II. Note.....	84
Alcohol Requirement of the Pure Food and Drug Law. Accuracy of Alcohol Assays of Pharmaceutical Preparations C. H. Briggs.....	29	Arkosite—Pigment and Filler. Note. S. P. Thatcher.....	83
Alcohol, Solid. Note.....	607	Arsenic, Soluble, in Mixtures of Lead Arsenate and Soap. H. V. Tartar and L. A. Bundy.....	561
Alcohol, Wood, Abstract of N. Y. State Factory Investigating Commission's Report by C. Baskerville.....	768	Ash in Coal, Preliminary Report of Am. Soc. T. M. and A. C. S. Committee. S. W. Parr.....	523
Alcohol, Wood, Editorial.....	712	Asphalt Specifications, Empirical Requirements in. Address. L. M. Law.....	1021
Alkali Inspector's Report for 1912, For England, Ireland and Wales, "Allophanoids" for Water Purification. Note.....	79	Assay Processes, U. S. P., Interpretation of. F. O. Taylor.....	601
Alloy for Reducing Electrical Losses in Bus-bar Joints. Note.....	425	Aubert, Alfred Bellamy—Obituary. W. F. Jackman.....	171
Alloys of Cobalt with Chromium, etc. E. Haynes.....	189	Austria-Hungary, Status of Chemical Industry. Note.....	424
Alloys of Lead, Tin, Antimony and Copper, Analysis of. D. J. Demorest.....	842	BACTERIA and Yeast, Influence of Ozone on. C. A. Nowak.....	668
Alsberg, Carl L. New Chief of Bureau of Chemistry. Note.....	170	Bakelite Patent Recognition. Note.....	619
Alumina and Aluminum from Mineral Silicates. A. H. Cowles.....	331	Barium Compounds, German Manufacture of. Consular Note. T. H. Norton.....	703
Alumina Production and Fixation of Nitrogen. S. A. Tucker.....	191	Barium Sulfate Precipitation. Apparatus for Unvarying Conditions. H. G. Smith.....	416
Aluminum Alloys. Note.....	1026	Battery Plates, Storage, Cadmium. Note.....	1028
Aluminum Industry in 1912. Note.....	606	Beehive Coke Ovens in the U. S. A. W. Belden.....	71
Aluminum Nitride, Serpek Process for Manufacture of. J. W. Richards.....	335	Beers, American, from Malt and Unmalted Cereals Examined by Use of Immersion Refractometer. R. Schwarz.....	660
Aluminum Plate, New Departures in. Note.....	337	Belgium, Chemical Activities. Note.....	161
American Chemical Journal to be Combined with the Journal of the American Chemical Society.....	958	Benzole as a Motor Fuel. Note.....	607
AMERICAN CHEMICAL SOCIETY.		Biochemistry, Chairman's Address at 48th Meeting A. C. S., Rochester. C. L. Alsberg.....	1019
Committee on Coal Analysis. Preliminary Report. W. A. Noyes, Chairman.....	517	Bisulfite Extraction of Zinc. Note.....	513
Committee Report, Centenary of Gas Industry. C. E. Munroe.....	81	Bitumen Pavements, Determination of Mineral Aggregate in. C. C. O'Loughlin.....	320
Division of Industrial Chemists and Chemical Engineers		Bitumens and Their Residuals. C. Richardson.....	462
New Descriptive Directory. A. Note. S. H. Salisbury, Jr.....	616	Bitumens, Effect of Exposure on. P. Hubbard and C. S. Reeve.....	15
47th (Spring) Meeting, Milwaukee, March 25 to 28, 1913.		Correction.....	260
Announcement.....	171	Bituminous and Resinous Substances, Classification. H. Abraham.....	11
Editorial.....	180	Boiler Scale, Effect of. Note.....	75
Program of Papers.....	342	Boiler Settings, New Design in. Note.....	864
48th (Annual) Meeting, Rochester, September 8 to 12, 1913.		Boilers, Steam, Heat Distribution in Operation of. P. Barker.....	670
Announcement.....	528	Book Reviews (see separate heading below).	
Editorial.....	712	Boron: Properties and Preparation. E. Weintraub.....	106
Program of Papers.....	868	Bouillon Cubes, Analyses of. F. C. Cook.....	989
Presidential Address. A. D. Little.....	793	Brass Recovered from Foundry Cinders. Note.....	512
Division Reports.....	956	Briquetting Fuel in the U. S. Note.....	607
Committee Reports, Fertilizer Chemistry Division.....	956	Briquetting Process, Scoria. Note.....	954
Sectional Meetings, Suggestion as to Programs for. B. C. Hesse.....	1020	Briquettes of Cast Iron Used in German Foundries. Note.....	513
Water, Sewerage and Sanitation Section to be Formed at Rochester Meeting. Note.....	702	Bromine, New Uses for, Wanted.....	780
American Chemist, What's the Matter with the? S. Born, 785; D. M. Grosh, 692; J. C. Hartzell, 871; Editorial, J. M. Matthews, 626; W. H. Watkins.....	785	Bureau of Chemistry, New Chief. A. Note.....	170
American Electrochemical Society. Research Fund. W. R. Whitney.....	432	Bureau of Mines: Coal Analyses. Editorial.....	883
23rd General Meeting, Atlantic City, April 3-5, 1913. Program.....	344	Mines Sanitation Section Organized. J. H. White.....	783
24th General Meeting, Denver, September 9-11, 1913. Program.....	870	Second Annual Report. Editorial.....	180
American Engineers Entertained in Germany. Note.....	783	Bureau of Standards' Analyzed Samples.....	528
American Institute of Chemical Engineers. Code of Ethics. Editorial	2	Burette for Nitrogen Work. F. C. Gephart.....	490
5th Annual Meeting, Detroit, December 4-7, 1912.....	49	Burner, Improved Laboratory. C. P. Fox.....	1019
Abstracts of Papers.....	50	Butter Fat and its Substitutes, Fluidity of. G. F. White and R. H. Twining.....	568
Patent Committee Report.....	51	Byrnes, Eugene A.—Obituary.....	870
6th Semi-Annual Meeting, Boston, June 25-28, 1913. Program.....	528	Book Reviews..... 84, 172, 260, 350, 437, 528, 620, 707, 786, 874, 961, 1030	
Presidential Address. T. B. Wagner.....	677	Air, Liquid,—Oxygen—Nitrogen, by Claude. G. B. Pegram.....	876
6th Annual Meeting, New York City, December 10-13, 1913.		Correction.....	1033
Program.....	1030	Allen's Commercial Organic Analysis VII. J. M. Nelson.....	1032
American Institute of Electrical Engineers. Resolutions Regarding Patent Legislation. Editorial.....	4	Alloys, Metallic: Their Structure and Constitution, by Gulliver. J. M. Lohr.....	874
Annual Convention, Cooperstown, N. Y., June 23-27, 1913.		American Ceramic Society. Transactions. Vol. XIV. A. V. Bleining.....	260
Abstracts of Papers.....	702	American Gas Institute Proceedings, 6th Annual Meeting. A. H. Elliot.....	437
American Mining Congress. Editorial.....	882		
American Petroleum Society. Organization.....	958		
American Society for Testing Materials and A. C. S. Committee on Coal Analysis. Preliminary Report. W. A. Noyes, Chairman.....	517		
Ammonia, Electrotechnical Production of. Note.....	75		

American Institute of Chemical Engineers, Transactions, Vol. IV. J. R. Withrow.....	84	Casein Industry. Note.....	59
Asphalts and Bitumens, Natural Rock, by Danby. H. Abraham.....	1032	"Cellophane," A "Viscose" Product. Note.....	515
Calcium Cyanamid, by Franke. F. K. Cameron.....	961	Celluloid Co., Sakai Plant, Japan. F. C. Axtell.....	38
Cane Sugar Industry, World's, by Geerlgs. W. D. Horne.....	85	Cement, Action of Alkali and Sea Water on. Note.....	1026
Cement Testing, Manual of, by Richards and North. R. K. Meade.....	707	Cement Clinker, Portland, Constitution of. E. D. Campbell.....	627
Chemical Industries of Belgium, Netherlands, Norway and Sweden, by Norton. W. A. Hamor.....	528	Cement Industry, Status of. Note.....	861
Chemical News, General Index, Vols. 1 to 100. L. E. Marrs.....	961	Cement, Portland. Control of Initial Setting Time. E. E. Ware.....	369
Chemical Technology and Metallurgy, by Neumann. J. H. James.....	173	Cerium Industry, Status of the. Note.....	610
Chloride of Lime in Sanitation, by Hooker. O. Kress.....	350	Chemical Engineer and Industrial Efficiency. W. M. Booth.....	237
Clay, The Natural History of, by Searle. A. V. Bleining.....	707	Chemical Engineering and the New Laboratories at Columbia Uni- versity. M. C. Whitaker and R. K. Murphy.....	304
Coal Analyses, U. S. Bureau of Mines. Editorial.....	883	Chemical Societies in N. Y. City. Program of Meetings, 1913-1914.....	870
Coal and the Prevention of Explosions and Fires in Mines, by Harger. E. G. Bailey.....	707	Chemical Trade of Germany. Note.....	1025
Coal, Its Composition, Analysis, Utilization and Valuation, by Somer- meier. E. G. Bailey.....	620	Chemists' Club, The Research Bureau. Editorial.....	268
Copper, Hydro-Metallurgy of, by Greenwalt. A. L. Walker.....	86	Chilean Mineral Deposits, Government Control of. Consular Note.....	873
Dictionary of Applied Chemistry, Vol. III, by Thorpe. M. C. Whitaker.....	620	Chlorine Cells, Billiter Alkali. Note.....	163
Disinfection and Disinfectants, by Christian. J. A. Deghué.....	876	Chlorine, Free, in Small Amounts Estimated Colorimetrically by Ortho-Tolidine. J. W. Ellms and S. J. Hauser.....	915
Electrochemistry, Principles of Applied, by Allmand. S. A. Tucker.....	529	Correction.....	1030
Electro-Plating and Analysis of Solutions, by Reama. S. A. Tucker.....	961	Chlorine Substitution Products of Methane from Natural Gas. C. Baskerville and H. S. Riederer.....	5
Electro-Plating, by Barclay and Hainsworth. S. A. Tucker.....	620	Chlorometer, The Rideal-Evans. Note.....	516
Explosives, by Brünswig. Translation by Munroe-Kebler. A. M. Comey.....	1032	Chromium Alloys with Cobalt, etc. E. Haynes.....	189
Fertilizer Handbook, The American, by Ware Bros. Co. L. E. Marrs.....	961	Chromium and Vanadium in Steel, Determination of. Correction. D. J. Demorest.....	84
Food Inspection and Analysis, by Leach. A. W. Thomas.....	621	Chromium in Steel, Colorimetric Determination. F. Garratt.....	298
Foods, Fatty, their Practical Examination, by Bolton and Revis. H. C. Sherman.....	787	Cinder and Soot Arrestor, A German. Note.....	696
Fuller's Earth. U. S. Bureau of Mines Bulletin, by Parsons. Note.....	1028	Clay, Plasticity of, J. Stewart.....	421
Furnaces and Refractories, by Howard. A. V. Bleining.....	262	Clay Products Industries in the U. S. in 1912. Geological Survey Note.....	874
Gas Analysis Methods (German), by Hempel. G. A. Burrell.....	787	Coal Analyses, U. S. Bureau of Mines. Editorial.....	883
Gasoline and Denatured Alcohol, Comparative Fuel Values in In- ternal Combustion Engines, by Strong and Stone. C. E. Lucke.....	173	Coal Analysis, Accuracy and Limitations of. A. C. Fieldner.....	270
General and Industrial Inorganic Chemistry, by Molinari. T. J. Parker.....	438	Coal Analysis: Preliminary Report for the Committee of the Ameri- can Society for Testing Materials and the American Chemical Society. W. A. Noyes, Chairman.....	517
Hydrosulfites (German), by Jelinek. J. M. Matthews.....	174	Coal, Determination of "Volatile." F. C. Weld.....	169
Hygiene, The Science of, by Pakes. D. D. Berolzheimer.....	262	Correction.....	260
Industrial and Manufacturing Chemistry, by Martin. H. C. Sher- man.....	1030	Coal Preparation, Technical Problems of. W. S. Ayres.....	68
Iron and Steel Analysis. Methods of American Rolling Mill Co., Middletown, O. W. Brady.....	620	Coal, Specific Heat of, and Its Relation to Combined Water in. H. C. Porter and G. B. Taylor.....	289
Iron and Steel, by Hudson and Bengough. W. Campbell.....	874	Coal Tar Dyes, Acid, Quantitative Separation of Mixtures of Certain. W. E. Mathewson.....	26
Lead and its Compounds, Chemical Analysis of, by Schaeffer and White. G. W. Thompson.....	351	Coal Tar Light Oil in the U. S. J. M. Weiss.....	61
Mineral Wastes, Notes on. Bureau of Mines, Bulletin 47, by Par- sons. Editorial.....	5	Cobalt Alloys with Chromium, etc. E. Haynes.....	189
Nitrogen, Utilization of Atmospheric, by Norton. W. A. Hamor.....	437	Cobalt Oxide Market. Note.....	251
Oil Industries, Chemistry of, by Southcombe. C. Ellis.....	1031	Coke-Oven Gases, Nitric Acid from. Note.....	75
Paint and Varnish Product, Analysis of, by Holley. P. C. McIlhenny.....	174	Coke Oven, Modern By-Product. Note.....	862
Paints, White Zinc, Preparation and Uses of, by Fleury. G. C. Stone.....	261	Coke Ovens, Beehive, of the U. S. A. W. Belden.....	71
Recipes, Formulas and Processes. Henley's 20th Century. R. K. Murphy.....	86	Coke Recovered from Ashes. Note.....	425
Refractories and Furnaces, by Havar. A. V. Bleining.....	262	Columbia University, Chemical Engineering and the New Labora- tories at. M. C. Whitaker and R. K. Murphy.....	304
Remedies, New and Non-official, 1911, by Press of American Medical Association. W. A. Hamor.....	707	Combustion Apparatus. Gas Bubble and Washing Tube. H. E. Smith.....	150
Rubber, Synthetic (German), by Rudolf Dittmar. T. Whittelsey.....	174	Combustion, Surface. Company Formed. H. Lieber.....	84
Service Chemistry, by Lewis and Brame. A. Smith.....	875	Combustion, Surface, Design of Appliances. C. E. Lucke.....	801
Sizing, Materials Used in, by Ermen. O. Kress.....	787	Correction.....	960
Soil Conditions and Plant Growth, by Russell. F. B. Carpenter.....	86	Combustion Tube, Clay Rubber Stoppers Eliminated. C. M. Johnson.....	581
Soil Fertility and Fertilizers, by Halligan. F. B. Carpenter.....	174	Concrete, Action of Various Substances on. R. K. Meade.....	723
Sugar Analysis, Handbook of, by Browne. W. D. Horne.....	172	Concrete Structures, Waterproofing of. Conclusions of Am. Soc. Testing Materials Committee. Note.....	1027
Water, Purification and Use in the Industries, by Christie. D. D. Jackson.....	351	Condenser, Reflux. S. W. Wiley.....	151
Works, Chemical, Their Design, Erection and Equipment, by Dyson and Clarkson. R. K. Murphy.....	786	Coöperation among Chemists and Manufacturers. Editorial. B. C. Hesse.....	92
CAFFEINE, Determination of Small Amounts. Comparison of Methods. B. L. Murray.....	668	Coöperation, Negative. Editorial.....	269
Calcium and Magnesium Titrated in Same Solution. P. J. Fox.....	910	Copper, Blue Gelatine. W. D. Bancroft and T. R. Briggs.....	9
Calcium Carbide and Acetylene, Industrial Uses of. Note.....	606	Copper Covered Steel. J. O. Handy.....	884
Calcium Carbide and Cyanamide Production in Norway. Note.....	251	Copper in Ores by the Sulfoeyanate Permanganate Method. D. J. Demorest.....	215
Calcium Carbide, Production of. Note.....	75	Copper in Ores Containing Arsenic, Antimony or Bismuth. Electro- lytic Determination. D. J. Demorest.....	216
Caloric Power of Coal. Preliminary Report of Am. Soc. T. M. and A. C. S. Committee. H. C. Dickinson.....	525	Copper in Steel—Influence on Corrosion. D. M. Buck.....	447
Camphor Exportations from Japan, 1910-1912. Note.....	775	Copper Refining, Electrolytic, in Norway. Consular Note.....	171
Camphor Production in Japan. Consular Note.....	436	Copper Wire Manufactured by Electrodeposition. Note.....	780
Caoutchouc, Production of. Note.....	76	Corn Products Industry. T. B. Wagner.....	677
Carbonates in Soils. Qualitative and Quantitative Methods. E. W. Gaither.....	138	Corrosion. Ajax Anti-Rust Sheets. Note.....	425
Carbon Black from Natural Gas. Note.....	696	Corrosion "Eliantite," an Acid Proof Alloy. Note.....	606
Carbon in Steels, etc. Use of Vitriified Clay Combustion Tube with Tapered Outlet. C. M. Johnson.....	488	Corrosion: Exposure Tests of Copper, Aluminum, etc., in England. Note.....	955
Carbon, Total, by Modified Parr Apparatus. C. E. Millar.....	234	Corrosion Minimized in Hot Water Supply Systems. Note.....	341
Carborundum Manufacture, Court Decision on. A Note.....	350	Corrosion of Iron and Steel. Editorial. W. H. Walker.....	444
		Corrosion of Iron and Steel. Electrolytic Prevention. J. K. Clem- ent and L. V. Walker.....	361
		Corrosion of Iron—Electrolytic Theory. Note.....	512
		Corrosion of Iron Imbedded in Clay. Influence of Cinders on. W. B. Schulte.....	554
		Corrosion of Iron. Influence of Various Elements. C. F. Burgess and J. Aston.....	458

Corrosion of Metals by Water..... A. T. Stuart.....	908	Fertilizers Containing Acid Phosphate and Calcium Cyanamid, De-	
Corrosion of Steel—Effect of Copper..... L. M. Buck.....	447	crease of Available Phosphoric Acid in..... R. N. Brackett.....	933
Crater Lake, Ore. Water Analysis..... W. Van Winkle and N. M. Fink.....	198	Fertilizers, Nitrogen, Consumption in Austria..... Note.....	698
Cresols, Thymol and Phenol, Rapid Volumetric Method for..... L. V. Rodman, A. I. Worth and F. P. Brock.....	831	Filter Paper, Swedish, Manufacture of..... Note.....	164
Crucible Holder, Improved Gooch..... L. H. Bailey.....	756	Filters, Pressure, for Clarifying Trade Wastes..... Note.....	428
Crude Fiber Estimation, An Improved Method of..... Note..... E. B. Forbes and J. E. Muesching.....	258	Filters, Pressure, New..... Note.....	79
Current Industrial News..... W. A. Hamor.....	74, 161, 251, 337, 423, 511, 605, 695, 774, 861, 950, 1022	Firebricks, Deterioration of, during Service..... G. Rigg.....	549
Cyanamid, Calcium as Cause of Decrease of Available Phosphoric Acid in Mixed Fertilizers..... R. N. Brackett.....	933	Fire Extinction on Ships by Use of Gases..... Note.....	162
Cyanamid, Manufacture and Uses..... E. J. Franke.....	159	Fireproofing of Cotton Goods, Permanent..... W. H. Perkin.....	57
Cyanamide Production, 1912-13..... Note.....	426	Fish Risks from Inflammable Liquids Lessened..... Note.....	164
DANIELS, F. H.—Obituary..... W. A. Hamor.....	871	Fish Scrap, Some Analyses..... J. R. Lindemuth and E. G. Parker.....	388
Daniels, William Willard—Obituary..... L. Kahlenberg.....	80	Flash-Point Testers, U. S. Bureau of Mines Modifications, Investigations with..... I. C. Allen and A. S. Crossfield.....	908
Datura—Assay of Individual Plants of Various Species..... F. A. Miller and J. W. Meader.....	1014	Flour and Gluten, Quantitative Estimation of Gliadin in..... G. A. Olson.....	917
Depreciation and Obsolescence..... R. K. Meade.....	762	Flour, Influence of Bran Extracts on Baking Qualities of..... H. L. White.....	990
Desiccator, Electric, for Analysis of Rubber and Organic Compounds..... L. J. D. Healy.....	489	Foods, Cooked Vegetable, Chemical Composition of, Part III..... K. I. Williams.....	653
Detonators and Safety Fuses..... Note.....	515	Correction.....	786
Dextrin, Production and Use..... Note.....	77	Food Standards and Their Effect upon Food Law Enforcement..... F. W. Robison.....	949
Diastase, Koji, Some Properties..... G. Kita.....	220	Forestry Service Investigations, U. S. Editorial..... C. C. Curtis.....	626
Dryer, The Gerlach..... Note.....	256	Formaldehyde, Total, in Fumigators and Commercial Solutions..... J. J. Hinman, Jr.....	752
Dyehouses and Bleach Works, General Efficiency in..... L. J. Matos.....	693	Fountain, Sanitary Drinking..... Note.....	954
Dyes, Acid Coal Tar, Quantitative Separation of Mixtures of Certain..... W. E. Mathewson.....	26	Fuel Briquetting in the U. S..... Note.....	607
Dye stuffs, Organic, Analysis of, International Sub-Commission..... Note..... F. Réverdin.....	259	Fuel, Motor—Benzole..... Note.....	607
EDITORIALS..... 2, 92, 180, 268, 356, 444, 534, 626, 712, 792, 882, 966		Fuel, Peat Powder as, for Locomotives..... Consular Note.....	786
Efficiency in Chemical Industries..... T. B. Wagner.....	677	Fuller's Earth..... Note on Dr. Parson's Bulletin.....	1028
Efficiency Studies—Hardwood Distillation Industry, Editorial..... L. F. Hawley.....	445	Fumes, "Dissipator" for..... Note.....	425
Electric and Gas Consumption in Greater New York in 1912..... Note.....	781	Fungicides: Studies on Lime Sulfur-Lead Arsenate Spray Mixture..... W. E. Ruth.....	847
Electric Furnaces, Device for Controlling Small..... C. B. Thwing.....	149	Fuses, Safety, and Detonators..... Note.....	515
Electric Heater for Laboratory Distillations..... L. T. Bryson.....	49	GAS and Electric Consumption in Greater New York in 1912..... Note.....	781
"Electrit," An Abrasive..... Note.....	79	Gas, Coal, Purification of..... Note.....	699
Electrochemical Industries of Italy..... Note.....	511	Gas-Engine Packing, Horton..... Note.....	611
Electrolysis from Stray Electric Currents..... Note.....	426	Gas Engines, A Novelty in..... Note.....	252
Electrolytic Method for Copper in Ores Containing Arsenic, Antimony or Bismuth..... D. J. Demorest.....	216	Gases, By-Product Coke Ovens, Production and Industrial Application..... J. Becker and L. B. Robertson.....	491
Electrolytic Method for Tin in Canned Foods..... A. S. Cushman and E. B. Wettengel.....	217	Gases, Compressed, Handling..... Note.....	76
Engineering Education, Society for Promotion of, Minneapolis Meeting.....	781	Gases for Fire Extinction on Ships..... Note.....	162
Ethyl Chloride, Chemistry of Anaesthetics, V..... C. Baskerville and W. A. Hamor.....	828	Gases Formed in Anaerobic Sewage Decomposition..... R. H. Jesse, Jr.....	636
Evans, William James, Chemists' Club Resolutions on Death of.....	783	Gases from Blast Furnace and Coke-Oven, Use of..... Note.....	254
Expert, Retained, Some Peculiar Functions of..... W. M. Grosvenor.....	772	Gases or Liquids: Indicator for Rate of Consumption..... Note.....	865
Explosives, Modified Form of Stability Test..... H. C. P. Weber.....	641	Gas, Illuminating, Hydrogen Sulfide in..... E. P. Harding and E. Johnson.....	836
Extraction Apparatus, Laboratory..... A. E. Perkins.....	148	Gas, Illuminating, Sulfur in..... R. S. McBride and E. R. Weaver.....	474
Extraction Apparatus, Modified..... G. M. MacNider.....	150	Gas, Illuminating, Testing Sulfate in Ammonium Sulfate Solution..... R. S. McBride and E. R. Weaver, 469; Correction.....	619
FARBWERKE vorm. Meister Lucius & Brüning, Semi-Centennial at Höchst a/M Germany..... Note.....	340	Gas Industry Centenary A. C. S. Committee Report..... C. E. Munroe.....	81
Fat, Butter, and its Substitutes, Fluidity of..... G. F. White and R. H. Twining.....	568	Gas Industry of England..... Note.....	699
Fat in Ice Cream..... H. F. Lichtenberg, Note..... H. C. Troy.....	786, 960	Gas Light and Coke Co., Beckton, London, England..... Note.....	862
Fat in Ice Cream, Modified Babcock for..... J. O. Halverson.....	403	Gas Mantles, Manufacture of..... Note.....	339
Fat in Ice Cream, Study of Modified Babcock Method..... J. O. Halverson.....	480	Gas Manufactured from Sewage Sludge..... Note.....	700
Fat in Ice Cream, Cereals and Chocolate..... E. P. Harding and G. Parkin.....	843	Gas, Natural, Chlorine Substitution Products of Methane from..... C. Baskerville and H. S. Riederer.....	5
Fatty Acids, Total, in Cotton-Seed Poots: Factory Determination..... F. N. Smalley.....	402	Gas, Natural, in Steam Boilers..... G. W. Barnes.....	486
Feeder, Automatic Chemical..... Note.....	950	Gas, Natural, Testing, for Gasoline Production..... E. S. Merriam and J. A. Birchby.....	824
Feldspar, Its Decomposition and Use in Fixation of Atmospheric Nitrogen..... W. H. Ross.....	725	Gas, Natural, Used in U. S..... Note.....	1029
Fermentologist, Training of..... C. A. Nowak.....	502	Gas, Producer, Analysis, Note on..... J. G. Vail.....	756
Fertilizer Chemistry Division A. C. S. J. E. Breckenridge, Secretary.....		Gas Producer and Engine, The Low..... Note.....	610
47th Meeting (Milwaukee) Report.....	431	Gas Purification, Efficiency of Oxides for..... A. F. Kunberger.....	580
Phosphate Rock, Standard Sample.....	344	Gas Scrubber, A New..... Note.....	517
48th Meeting (Rochester), Report.....	956	Gas, Water, Composition of..... Note.....	867
Chairman's Address..... P. Rudnick.....	948	Gasoline, Condensation of, from Natural Gas..... G. A. Burrell and F. M. Seibert.....	895
Fertilizer Legislation Committee Report..... F. B. Carpenter.....	957	Gasoline Gas Generator for Sulfur Determinations..... C. E. Waters.....	853
Phosphate Rock Committee Report..... F. B. Carpenter.....	957	Gasoline Production, Testing Natural Gas for..... E. S. Merriam and J. A. Birchby.....	824
Phosphoric Acid Committee Report..... G. Farnham.....	956	Gasoline Substitute, A New—"Parol"..... Note.....	607
Fertilizer Industry of Charleston, S. C..... Note.....	698	Gasoline Substitutes..... Note.....	514
Fertilizer, Sponges as..... J. G. Smith.....	850	Gauge for Liquid Levels.....	516
Fertilizer—Use of Waste Sulfate Liquor..... Note.....	513	Gelatin in Sour Cream..... A. Seidenberg.....	927
Fertilizers, Ammonia by Folin's Method..... O. Folin and A. W. Bosworth.....	485	Geological Survey Building Provided..... Note.....	350
		Glass Bottle and Hollow Ware Industries in U. S..... Note.....	951
		Glass Industry, Window, Present Status..... Note.....	80
		Glass Plate Industry in the U. S..... Note.....	253
		Glass, Window, Japanese..... Note.....	75
		Gliadin in Flour and Gluten..... G. A. Olson.....	917
		Glucose, Confectioners', Analyses of..... E. Gudeman.....	665
		Glues, Improved Jelly-Strength Apparatus..... E. C. Hulbert.....	235
		Glycerine, Crude, On Methods of Analysis of..... E. A. Ray.....	784
		A. C. Langmuir.....	871
		Glycerins, Soap Lye and Saponification Crude..... Note.....	77

Gold and Platinum by the Ton. Note.....	1029	Lead, Corrosion of. R. H. Gaines.....	766
Gold Precipitated by Manganous Salts. A. D. Brokaw.....	560	Lead Paints, Toxicity of. Note.....	513
Graphite, Colloidal, Lubrication with Oils and with. C. F. Mabery.....	717	Lead Poisoning. Note. M. Toch.....	434
Greases, Melting Points, by N. Y. Testing Laboratory Viscosimeter. H. W. Mahr.....	674	Leather, Artificial, from "Soylont." Note.....	514
HOPS from different Parts of World. H. V. Tartar and B. Pilkington.....	478	Leather, Sole, Composition of Some. Note.....	608
Horn Substitute from Leather and Celluloid. Note.....	608	Lechtin and Albumin Industry. Note.....	340
Hot Water Supply Systems to Minimize Corrosion. Note.....	341	Lewkowitzsch, Julius—Obituary.....	959
Humin for Purification of Sugar Factory Waste Waters. Note.....	515	Lime in Cow Feces, Determination of. R. A. Dutcher.....	37
Humus in Hawaiian Soils by Ammonium Carbonate Method. J. B. Rather.....	222	Correction.....	260
Humus, Nitrogen in. C. B. Lipman and H. F. Pressey.....	143	Lime for Water Purification. Note.....	75
Humus, Proposed Modification of Official Determination. O. C. Smith.....	35	Lime Requirement of Soils, Estimation of. J. A. Bizzell and T. L. Lyon.....	1011
Hydrocarbons of Utah. C. Bardwell, B. A. Berryman, T. B. Brighton and K. D. Kuhre.....	973	Limestone, Syrian Autoburning. C. P. Fox.....	1029
"Hydro-Cator." Gauge for Liquid Levels. Note.....	516	Lime-Sulfur, Commercial, Microorganisms in. C. A. Peters and A. W. Brooks.....	1013
Hydrogenation of Oils. C. Ellis.....	95	Liquefied Gases Used in Mining and Metallurgy. Note.....	606
Hydrogen Sulfide in Illuminating Gas, Apparatus and Method for. E. P. Harding and E. Johnson.....	836	Loeb: Morris Loeb's Will. Editorial.....	2
Hypochlorite, Calcium, Examples of Efficiency of, in Treating Turbid Waters. E. Bartow.....	18	Lubrication with Oils and with Colloidal Graphite. C. F. Mabery.....	717
Hypochlorite Disinfection, Cost of. Note.....	255	MAINE , Industrial Future of. Note.....	74
Hypochlorite Disinfection of Baltimore Water Supply. J. B. Thomas and E. A. Sandman.....	476	Magnesite in Lower California. Consular Note.....	259
IGNITIONS , Analytical, Convenient Device for. E. D. Campbell.....	675	Magnesium and Calcium Titrated in the Same Solution. P. J. Fox.....	910
Index to Chemical Literature by U. S. Patent Office. Editorial. L. H. Baekeland.....	534	Management, Scientific, and the Chemist. H. W. Gillett.....	593
Industrial Chemists and Chemical Engineers Division A. C. S., S. H. Salisbury, Jr., Secretary.....	430	Management, The Art of Industrial. Editorial.....	93
47th Meeting (Milwaukee), Report.....	956	Manganese Content of Raw Linseed Oil. E. W. Boughton.....	282
48th Meeting (Rochester), Report.....	946	Manganese in Rock, Slags, Ores and Spiegels. F. J. Metzger and L. E. Marrs.....	125
Industrial Prosperity, Relation of Big Business to, with Special Reference to Mining. C. R. Van Hise.....	607	Manganous Salts Precipitate Gold. A. D. Brokaw.....	560
Inflammable Liquids, Storage of. Note.....	426	Maple Products, Analysis of. I. Electrical Conductivity Test for Purity of Maple Syrup. J. F. Snell.....	740
Injector, Fitting, "Dea." Note.....	51	II. Comparative Study of the Delicacy of Methods. J. F. Snell and J. M. Scott.....	993
Intellectual Property, Protection of. L. H. Baekeland.....	703	Market Report.....90, 178, 266, 354, 442, 532, 624, 710, 790, 880, 964.....	1036
International Association of Chemical Societies, Solvay Gift to. Note.....	344	Match Industry of Sweden. Note.....	511
International Congress of Applied Chemistry, 8th Secretary's Report. B. C. Hesse.....	348	Meat, Frozen, Industry of New Zealand, Chemistry in Relation to. A. M. Wright.....	673
Final Shipment of Reports, Vols. 25-29.....	429	Melting-Point Apparatus for Substances of Indefinite Melting Point. A. P. Bjerregaard.....	938
Official Closing.....	321	Melting Points of Elements of Atomic Weight 48 to 59. Note.....	780
International Congresses of Applied Chemistry, The Problem of. B. C. Hesse.....	782	Menhaden Industry. J. W. Turrentine.....	378
International Engineering Congress, 1915. Announcement.....	339	Metallic Pigments. D. Davidson.....	83
Iodine Industry. Note.....	484	Metallizing Process, The Schoop. Note.....	776
Iodine Tincture. L. F. Kebler.....	955	Metal Statistics for 1912, U. S. Note.....	161
Iron and Steel Coated with Lead Electrolytically. Note.....	444	Metal Trade, Foreign, of U. S. in 1912. Note.....	424
Iron and Steel Corrosion. Editorial. W. H. Walker.....	361	Metal Trade in 1912, British. Note.....	252
Iron and Steel Corrosion. Electrolytic Prevention. J. K. Clement and L. V. Walker.....	839	Metals, Intergranular Cement. W. E. Ruder.....	452
Iron and Steel, Fusion Method for Sulfur in. F. H. Franklin.....	357	Meter, Recording Flow Rate, New Type of, and Recording Differential Pressure Gauge. Note.....	610
Iron and Steel Industry. Some Developments of. Editorial. G. D. Chamberlain.....	528	Micarta and Bakelite Micarta. Note.....	950
Iron and Steel Institute Fellowship Awarded. Note.....	252	Milk, Analysis of Unsweetened Evaporated. C. A. A. Utt.....	168
Iron and Steel in 1912. Statistics. Note.....	123	Milk, Calculating Fat-free Residue of. H. C. Troy.....	872
Iron and Steel. Oxygen Determination. R. H. McMillen.....	349	Milk-Fat in Evaporated Milk and Milk Powders. E. P. Harding and G. Parkin.....	131
Iron and Steel, Protection by Paint Films. N. A. Dubois.....	968	Milk, Mass., Quality of. H. C. Lythgoe.....	922
Iron and Steel, Titanium in, by Colorimetric Method. C. R. McCabe. Note.....	735	Milk, Watered, Properties of. E. W. Long and C. E. May.....	573
Iron Carbide in Presence of Silicon, Influence of Sulfur on Stability of. Note.....	872	Mine Gas Problems. G. A. Burrell.....	181
Iron Castings to Resist Corrosion. Note.....	605	Mineral Production of Canada. Canadian Mines Report.....	436
Iron, Cast: Use of Briquetts in German Foundries. Note.....	867	Mineral Production of Sweden. Official Report for 1912. Note.....	866
Iron, Charcoal, Increased Use of. Note.....	513	Mineral Waste. Editorial.....	5
Iron Corrosion—Electrolytic Theory. Note.....	161	Mine Safety Association, American Society Formed.....	258
Iron Corrosion, Influence of Various Elements. C. F. Burgess and J. Aston.....	512	Mining Industry Needs. J. F. Callbreath.....	236
Iron Corrosion, Influence of Various Elements. C. F. Burgess and J. Aston.....	458	Mining, Relation of Big Business to Industrial Prosperity with Special Reference to. C. R. Van Hise.....	946
Iron Imbedded in Clay, Influence of Cinders on the Corrosion of. W. B. Schulte.....	554	Moisture in Coal. Preliminary Report of Am. Soc. T. M. and A. C. S. Committee. W. F. Hillebrand.....	521
Iron Pyrites, Plant for Treatment of. Note.....	697	NAPHTHALENE , New Uses for. Note.....	337
Iron, Raw, German Record Production. Consular Note.....	706	Naval Stores Industry. C. H. Herty.....	65
KELPS , Pacific Coast, Analyses. E. G. Parker and J. R. Lindemuth.....	287	Negative Coöperation. Editorial.....	269
LABORATORY and Plant.....	38, 144, 223, 304, 416, 486, 578, 670, 755, 850, 935, 1017.....	Nelsonite, Possible Commercial Utilization of. W. H. Waggaman.....	730
Laboratory, Chemical, of the Picher Lead Co. J. A. Schaeffer.....	850	"Neradol D," A Synthetic Tannin. Note.....	863
Lamp Bulbs Exhausted at High Temperatures. Note.....	1028	New Publications. D. D. Berolzheimer.....	1033
Lards, Effects of Feeds on the Properties of. H. C. L. Hare.....	41087, 175, 263, 352, 439, 529, 622, 708, 788, 877, 962.....	1033
Lead Arsenate and Soap Mixtures, Soluble Arsenic in. H. V. Tartar and L. A. Bundy.....	561	Nichols-Hesse Dinner. Editorial.....	268
Lead Coating of Iron and Steel, Electrolytic. Note.....	955	Nickel a By-Product in the U. S. Note.....	1024

Nitrous Acid and Urea. Rate of Reaction in Dilute Solutions. W. D. Bonner and E. S. Bishop	141
Notes and Correspondence	
..... 80, 167, 257, 349, 431, 616, 703, 783, 821, 989, 1029	
OBITUARIES	
Ogier, Jules. Obituary	80, 171, 432, 616, 870, 989, 1030
Oil. Coal-Tar Light in the U. S. J. M. Weiss	1030
Oil from Hickory Nuts. G. O. Peterson and E. H. S. Bailey	61
Oil Fuel, Scottish, for British Navy. Trade Note	739
Oil. Kukui (Candle Nut) A. R. Thompson	873
Oil Industry, Mineral, Some Developments. Note	644
Oil Industry, Scottish Shale, Condition of. Note	339
Oil. Investigations with U. S. Bureau of Mines Modifications of Flash Point Testers. I. C. Allen and A. S. Crossfield	701
Oil. Linseed, Effect of Certain Pigments on Note on Manganese Content of Raw. E. W. Boughton	908
Oil. Linseed. Oxygen Absorption Test. H. Mannhardt	282
Oil. Linseed, World's Shipments. Note	129
Oil. Peanut, Nitrobenzol in. H. J. Lucas	423
Oil. Peppermint, Industry in Japan. Y. Shinosaki	576
Oil. Peppermint, Japanese. Y. Shinosaki	656
Oil. Pine Nut. M. Adams and A. Holmes	658
Oil Shales, American. C. Baskerville	285
Oil. Whale, A New Product from, by Hydrogenation. Note	73
Oils. Antiseptic Tests of Wood Preserving. A. L. Dean and C. R. Downs	608
Oils. "Hardened." Note	126
Oils, Hydrogenation of. C. Ellis	427
Oils, Lubrication with, and with Colloidal Graphite. C. F. Mabery	95
Oils, Mineral Lubricating and Transformer, Evaporation Test for. C. E. Waters	717
Oils, Raw Paint, Drying Rates of, Comparison. L. V. Redman, F. P. Brock and A. J. Weith	394
Oils, Tars and Pitches, Methods for Testing. S. R. Church	630
Olive Oil Imports not Adulterated. U. S. Dept. Agric. Note	195
Organic Compounds Estimated by Potassium Permanganate. C. M. Pence	706
Original Papers.....S. 95, 181, 270, 361, 447, 535, 627, 713, 801, 884, 968	218
Orsat Apparatus, New Form. A. Note. J. M. Camp	968
Oven, Drying, Automatic Electric. Note	84
Oxygen, Consumption of. Note	866
Oxygen in Iron and Steel. Use of Electric Resistance Furnace for Determination. R. H. McMillen	695
Criticism. A. S. Cushman	123
Oxygen in Tungsten Powder and in Steel, Determination of. C. M. Johnson	349
Oxygen in Water, Winkler's Method for; Effect of Nitrite and Its Prevention. F. E. Hale and T. W. Melia	295
Ozone. Editorial. A. M. Buswell	976
Ozone, Influence of, on Yeast and Bacteria. C. A. Nowak	882
PACKING, Horton Gas Engine. Note	668
Packing-House Discharges, Disposed of. Note	611
Paint as an Engineering Material. M. Toch	514
Paint Films, Protection of Iron and Steel by. N. A. Dubois	366
Painting of Steel Passenger Coaches. Note	968
Paint Oils, Raw, Drying Rates of, Comparison. L. V. Redman, F. P. Brock and A. J. Weith	425
Paints and Varnishes. Practical Accelerated Test. A. M. Muckenfuss	630
Paints for Indicating Uses of Pipes. Note. M. Toch	535
Paints for Steel Exposed to Air and Fresh Water, Alternately. P. H. Walker and S. S. Voorhees	784
Paints, Lead, Toxicity of. Note	899
Paper and Pulp Industry, Governments' Interests in. M. L. Griffin	513
Paper and Pulp, List of U. S. Public Documents on. H. E. Surface	500
Paper from Seaweed. Note	614
Paper Industry in Norway and Sweden. Note	786
Paper Industry of Austria-Hungary. Note	337
Paper Industry of Japan. Note	867
Paper Industry, Some Innovations in	255
Papermaking, Progress of, in 1912	781
Paper: New Chemical Process for Fiber. Note	340
Paper, Polarimetric Method for Starch in. C. E. G. Porst and H. A. Crown	1028
Paper Pulp from Longleaf Pine by Soda and Sulfate Processes. S. D. Wells	304
Paper, Quantitative Determination of Rosin in. C. F. Sammet	906
Note on. M. L. Griffin	732
Paper: Testing the Liquor in Sulfite Cooks. Note	960
"Parol," a New Gasoline Substitute. Note	951
Parr Total Carbon Apparatus, A Modification. C. E. Millar	607
Patent Expert, The, and the Chemical Manufacturer. B. C. Hesse	234
Patent Legislation, American Institute of Electrical Engineers' Resolutions Regarding. Editorial	854
Patent Office, U. S., Comments on Report of Investigation of. L. H. Backeland	4
Patent System, U. S., Relation of Manufacturer to. W. M. Grosvenor	417
Patents (See separate heading below)	685
Patents. Protection of Intellectual Property. L. H. Backeland	51
Peat as Fuel. C. A. Davis	704
Pent Powder as Fuel for Locomotives. Consular Note	786
Peppers, Red, Composition of Different Varieties. I. M. Tolman and L. C. Mitchell	747
Peppin and Peptase, Some Distinctions between. R. Wahl	752
PERKIN MEDAL AWARD	241
Address of Acceptance. James Gayley	241
Dr. Gayley's Interest in Education. Address. E. Hart	247
Presentation Address. C. F. Chandler	241
The New Age. Address. R. W. Raymond	249
The Value of Expert Opinions. Address. H. M. Howe	246
Perkin Medal, The. Editorial	180
Petrol, Catalytic Production of. Note	774
Petroleum Analytical Methods. S. P. Sadler	393
Petroleum Industry, Caucasian during 1912. Note	701
Petroleum Industry in 1912, U. S. Note	253
Petroleum Output in 1912, World's. Note	340
Petroleum Production in 1912. Geological Survey Note	872
Pharmacopoeia, U. S., Progress of 9th Revision. J. P. Remington	429
Phenol: Effect of Temperature, Acid Concentration and Time on Bromination in Quantitative Determinations. L. V. Redman, A. J. Weith and F. P. Brock	389
Phenolic Condensation Products, Resinous, The Chemical Constitution of. Address of Acceptance. Willard Gibbs Medal Award, 1913. L. H. Backeland, 506; Correction	620
Phenol, Thymol and Cresols, Rapid Volumetric Method for. L. V. Redman, A. J. Weith and F. P. Brock	831
Phosphate, Florida Production in 1912. Note	425
Phosphate Rock, Committee Report, Fertilizer Division A. C. S. 48th Meeting, Rochester. F. B. Carpenter	957
Phosphate Rock, Standard Sample of. Division of Fertilizer Chemistry, A. C. S.	344
Phosphates in Surface Waters. G. S. Jamieson	301
Phosphates Reinforced by Fermenting Manure. W. E. Tottingham and C. Hoffman	199
Phosphoric Acid, Committee Report. Fertilizer Division A. C. S. 48th Meeting, Rochester. G. Farnham	956
Phosphoric Acid, Decrease of Available in Fertilizers Containing Acid Phosphate and Calcium Cyanamid. R. N. Brackett	933
Phosphoric Acid Determination, Study of Pemberton-Kilgore Method. P. L. Hibbard	998
Phosphoric Acid, Soil, Insoluble in Hydrochloric Acid, Condition of. W. H. Fry	664
Phosphorus Determination in Ferro-Tungsten, Tungsten Powder, Tungsten Oxide and Tungstic Acid by Direct Solution. C. M. Johnson	297
Phosphorus Determination in Steels Containing Vanadium. J. R. Cain and F. H. Tucker	647
Phosphorus in Vanadium Steel and Ferrovandium. C. F. Sidener and P. M. Skarvold	838
Picher Lead Co. Chemical Laboratory. J. A. Schaeffer	850
Pigments, Effect of, on Linseed Oil. E. W. Boughton	282
Pigments, Metallic. D. Davidson	83
Pigments, Testing Opacity and Hiding Power. G. W. Thompson	120
Pipes, Paints for Indicating Uses of. Note	609
Pipette, An Automatic. C. H. McCharles	755
Platinum, American Placer, Iridium in. Note	74
Platinum and Gold by the Ton. Note	1029
Platinum Crucibles: Life Lengthened by use of Méker Burner. R. J. Wysox	705
Platinum Market in June, 1913. Note	697
Platinum Production. Geological Survey Note	960, 1029
Platinum, Reinforced. Note	74
Platinum Substitute—Tantalum. Note	162
Platinum Thief. A Note. R. J. Wysox	82, 259
L. Selmi	528
Potash Committee, Fertilizer Division A. C. S. Milwaukee Meeting. J. E. Breckenridge, Ch.	431
Potash Deposits, American, Development of. Note	698
Potash from Feldspar. Note	338
Potash from Seaweed in Mexico. Note	338
Potash Industry, German, Crisis in. Consular Note	706
Potash Lands Withdrawn. Geological Survey Note	350
Potash, Leaching of, from Freshly Cut Kelp. A. R. Merz and J. R. Lindenmuth	729
Potash Situation in Austria. Note	513
Potassium Determined by Rapid Modified Chlorplatinate Method. W. B. Hicks	650
Potassium Salts from Seaweed. Note	251

Power from Waste Heat. Consular Note.....	706	Formic Acid. Walker.....	264; Weise, 89
Power Plants. Estimates on Cost. Note.....	515	Gas-Analyzer, Automatic. Mertens.....	623
Pressure Gauge, Recording Differential, New Type of, and Recording Flow-Rate Meter. Note.....	610	Gases, Mixed, Liquefied, Separating. Morrison.....	531
"Progressive Age" Becomes "Gas Age." Note.....	171	Gases Obtained Economically. Acker.....	265
Projection Experiments with Spectra. H. E. Howe.....	578	Gases, Waste of Combustion from Cement Kilns Utilized. Schott.....	789
Public Utilities, Control of. Editorial. W. A. Hamor.....	967	Gasoline Manufacture. Burton.....	264
Pulp and Paper, List of U. S. Public Documents on. H. E. Surface.....	614	Gasoline, Natural Gas, Refining. Snelling.....	531
Pulp, etc., from Waste Resinous Woods. Note.....	427	Glue or Gelatin. Upton.....	709
Pulverizer, New Type of. Note.....	609	Gold Pigment. Hasburg.....	531
Pump, Explosive, Art, Recent Activity in. Note.....	776	Hydrogenation, Process of. Ellis.....	88
Pump, New Centrifugal. Note.....	951	Hydrogenized Products from Unsaturated Compounds. Skita.....	789
Pyrites Cinder, Rapid Determination of Sulfur in. A. B. Conner.....	399	Hydrogen Peroxide, Solidified. Stockelbach.....	353
		Indigo, Synthetic, New Form of. Schmidt and Steindorff.....	531
		Iron and Steel Making. Billings.....	1035
Patents, United States		Iron and Steel Metallurgy. Simpson and Oviatt.....	709
.....88, 176, 264, 353, 440, 531, 623, 709, 789, 878, 963, 1034		Iron and Steel Refined by Ferrochromium Alloy. Buchel.....	1034
Acetate of Lime and Wood Alcohol. Volney.....	353	Iron and Sulfuric Acid from Ferrous-Sulfate Sludge. Weeks.....	264
Acetone and Higher Alcohols by Fermentation of Starch, Sugars, etc. Fernbach and Strange.....	176	Iron, etc., Treated to Prevent Corrosion. Richards.....	879
Albumin Powder, Soluble. Bass.....	878	Iron, Malleable, Direct from Ore. Lindblad.....	531
Alcohol. Keifer.....	88	Iron Ores, Smelting. McClenahan.....	879
Alcohol from Sulfite Liquor. Ekström.....	88, 177, 265	Iron Oxid Regenerated in Gas Purification. McDonald.....	709
Alcohol Regained from Fermenting Vats. Zeckendorf.....	265	Joint, Expansion, A Self-Equalizing.....	609
Alumina and Sulfate of Potash. Chappell.....	963	Leading and Tinning Metals. Plathner and Dorn.....	709
Aluminate, Sodic-Silico and Hydrochloric Acid. Cowles.....	88	Lime, Hydrated; Heat of Hydration Utilized. Doherty.....	878
Aluminum Extracted from its Ores. Kiscock.....	440	Malt Manufacture. Wahl.....	879
Aluminum Nitrid. Serpek.....	623	Metal-Bearing Solutions Treated. Ashcroft.....	1034
Ammonia, Process of Making. Bosch and Mittasch.....	440	Metals, Alloys and Steels, Treating Melted. Baraduc-Muller.....	963
Ammonia, Purified, from Coal Gas. Tufts.....	789	Metals, Clad, Production of. Page.....	878
Ammonium Compounds. Steinmetz.....	709	Metals, Precious, Extracted from their Ores. Williams.....	441
Asbestos Purified. Arsem.....	264	Nickel Alloys, Low-Carbon. Byrnes.....	531
Asphalt Making. Dundas.....	441	Nitrate of Lime and Dicalcium Phosphate in One Operation. Peacock.....	531
Asphalt Production. Burton.....	441	Nitric Acid. Moest and von Berneck.....	264
Baking Powder. Jacoby.....	531; Klapproth, 709	Nitric Acid, Concentrated. Moest and von Berneck.....	264; Pauling, 1035
Barium Salts, Soluble. Hunt.....	963	Nitric and Sulfuric Anhydrids, Solid Compound. Schultze.....	177
Barytes Separated from Ores. Greenstreet.....	879	Nitrogen Compounds. Pettibone and von Sholly.....	89
Bleaching Vegetable Fiber and Fabrics. Gruter.....	789	Nitrogen Compounds, Including Nitrids and Ammonia. Sinding-Larsen.....	89
Bromin or Bromids, Production of. duPont.....	789	Nitrogenous Compounds Made. Greenstreet.....	440
Butter-fat in Butter, Determination. Shaw.....	353	Oils, Cleaned and Refined. Stone.....	963
Butter Substitute, Hydrogenated. Ellis.....	88	Oils, Catalyst for Hydrogenating, etc. Ellis.....	623
Camphor from Borneol and Isoborneol. Ruder.....	878	Oils Extracted from Fuller's Earth. Felizat.....	963
Caoutchouc Substances, Process of Making. Harries.....	531, 1034	Ore Treatment. Schick.....	353
Carbon, Granular. Lee.....	963	Ore Treatment Preparatory to Magnetic Separation. Etherington.....	440
Carbon or Lampblack Production. Fernekes.....	879	Ores, Magnetic Separation of, from Slime. Schwerin.....	789
Carbon Treatment, etc. Smith.....	879	Ores, Roasting and Recovering Zinc. Reed.....	879
Catalyzer for Hydrogenating Oils, etc. Ellis.....	623	Oxalates, Making of. Hempel.....	963; Andrews, 878
Catalyzers, Minutely Divided. Kast.....	963	Oxidizing or Reducing by Electrolysis. Kolsky.....	88
Cellulose Compound, Non-Inflammable. Lindsay.....	264, 353	Permutit Revivified or Restored. Schweikert.....	440
Cellulose Manufacture. Loomis.....	353	Persulfates. Adolph and Pietzsch.....	623
Cement-burning Kiln. Edison.....	878	Phosphate, Dicalcium and Nitrate of Lime in One Operation. Peacock.....	531
Cement Clinker and Potash. Gelléri.....	623	Phosphoric Acid, Available. Connor.....	89
Cement, Portland. Edison.....	623	Phosphoric Acid from Mineral Phosphates. Washburn.....	177
Cement, Portland. Richards.....	1035	Phosphorus and Sulphur Removed from Iron, etc. Greene.....	878
Cement Steel. Benjamin.....	440	Pitch from Coal-Tar, Petroleum Residues, Creosote, etc. Hennebutte.....	89
Chemical Reaction by Means of Electric Arc. Hayden.....	878	Plastic or Elastic Substance. Stockhausen.....	709
Citric Acid Production. Zaborski.....	878	Potash Alum. Hart.....	709
Coke from Wood-Tar. Lefelmann.....	789	Potash and Cement Clinker. Gelléri.....	623
Coke, Purifying. Simpson.....	177	Potash, Iodine and Chlorine from Seaweeds. Cameron and Moore.....	265
Contact Masses, Regenerating. Kelsey.....	177	Potash Salts from Feldspar. Bassett.....	963
Concrete Waterproofed. Horn.....	264	Potash, Sulfate of, and Alumina. Chappell.....	963
Copper Electrolytically Refined. Van Arsdale.....	879	Potassium Salts from Feldspar. Morse and Sargent.....	88
Copper Ores Bearing Precious Metals, Treatment of. Clancy.....	531	Red Lead—Product from which it can be Burnt. Jansen.....	440
Copper Separated from Other Metals. Edison.....	265	Reducing Chemical Compounds. Weintraub.....	176
Corrosion Prevented by Treatment of Iron, etc. Richards.....	879	Reducing or Oxidizing by Electrolysis. Kolsky.....	88
Cyanid Solutions, Precipitation of Material from. Merrill.....	789	Rubber, Attaching to Metals. Daft.....	88
Cyanids, Alkali Metal. Kendall.....	88	Rubber Goods. Windsor-Richards.....	879
Cyanogen Compounds. Acker.....	1034	Rubber-Like Compounds. Holt.....	709
Diastatic Product. Takamime.....	440	Rust Proofing Iron, Steel, etc. Bontempi.....	1034
Edible Oils, Process of Making. C. Ellis.....	353	Salt Manufacture. Webster.....	353
Electric-Furnace Lining. Becket.....	264	Seaweeds Source of Potash, Iodine and Chlorine. Cameron and Moore.....	265
Electrochemical Process. Hayden.....	1035	Shellac, Refined. Cassard.....	879
Electrode, Luminous or Flaming. Hayden.....	264	Silicidizing Articles Containing Carbon. Tone.....	440
Electrolysis. Du Bois.....	10	Silicon Carbide. Tone.....	176
Engines, Gasoline, Removing Carbon from. Elliott and Kelly.....	88	Smelter Gases, Obtaining Sulphur from. Sanborn, McMahon, Overbury and Young.....	709
Explosive. Imperiali.....	440; O'Brien, 963, 1034; Raschig, 963	Soda Liquors, Treatment of Waste. Neil.....	177
Fats and Oils, Decomposition of. Reuter.....	879	Soda Pulp-Mills, Precipitating Ulmic Compounds from Black Liquors. Langlet.....	709
Fats, Bleaching Solid and Semisolid. Richter and von Orth.....	963	Sodium, Light Metals. Seward, von Kugelgen and von Bidder.....	176
Fatty Food Product, Hydrogenated. Ellis.....	879	Stannic Chloride. Doerflinger.....	441
Ferric Chloride Made. Dow and Schaefer.....	440	Stannic Oxid, Reduction of. Metzl.....	353
Ferro-Alloys, Low-Carbon. Morehead.....	709		
Ferrosilicon by Reduction. Byrnes.....	265		
Fertilizer, Ammonium Superphosphate. Wilson and Haff.....	709		
Fertilizer Manufactured. Slater.....	879		
Flour, Improving Condition of. Wesener.....	963		
Formaldehyde Manufacture. Kusnezow.....	879		

Patents, United States (Continued)

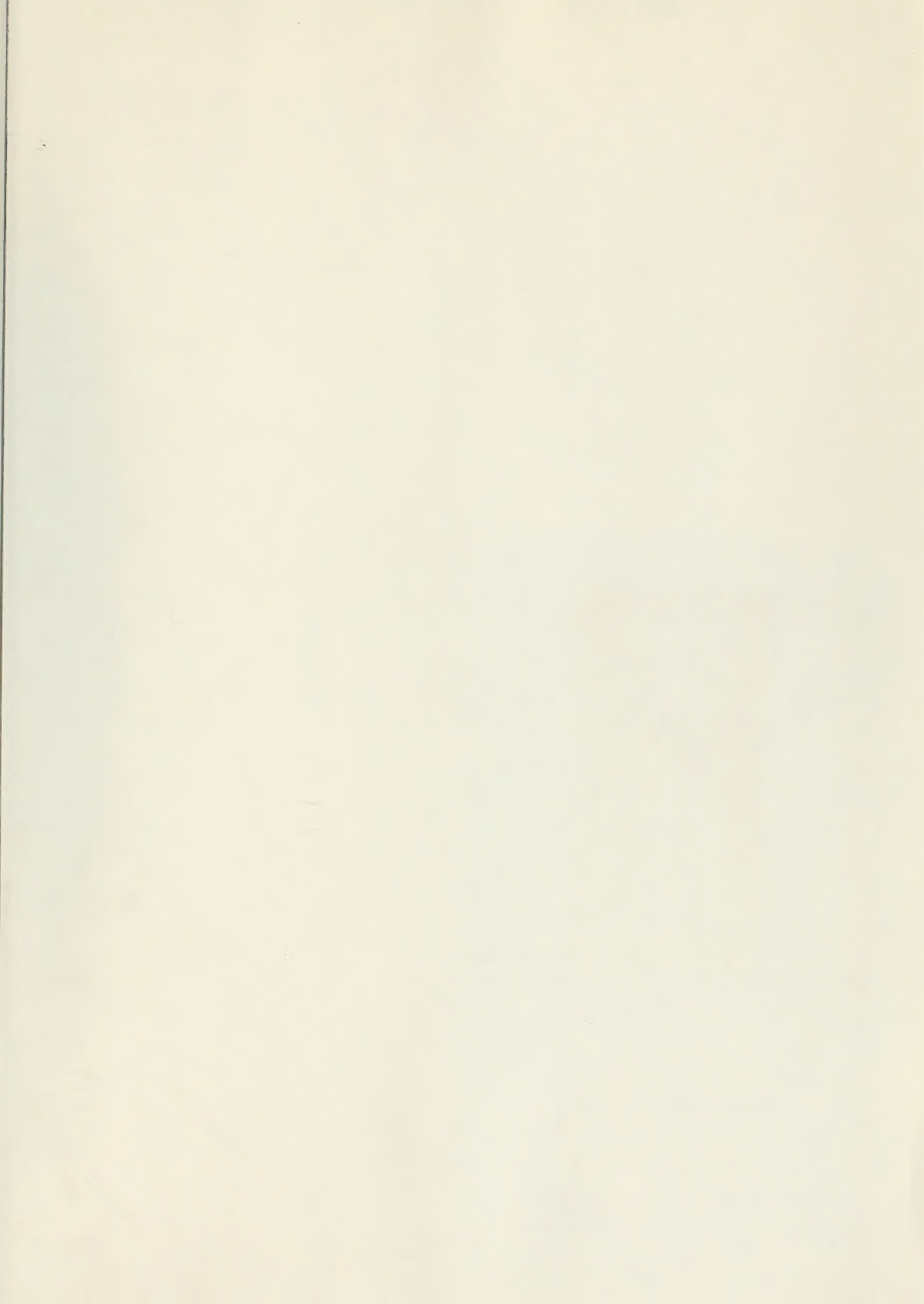
Starch, Treatment of	Neuberger and Bergh	177
Steel, Iron, etc.	Machlet	789
Steel Process	Churchward	879
Stone, Artificial	Turner	879
Sugar Refining	Wiese	453
Sugar, Refining Brown	Lundgren and Gerling	789
Sugar, White, Direct from Raw Juices	Wynberg and Sauer	963
Sulfid Ore Treatment	Titus and Barendseher	879
Sulfid Ores, Treatment	Banes	1035
Sulfite Liquor, Alcohol from	Ekstrom	88, 177, 265
Sulfite Waste Explosives	Raschig	531
Sulfite Waste Liquor, Concentrating	Ellis	531
Sulfur from Smelter Gases	Samborn, McMahon, Overbury and Young	878
Sulfur and Phosphorus Removed from Iron, etc.	Greene	709
Sulfur, Suspensible	Hillyer	264
Sulfuric Acid and Iron from Ferrous Sulfate Sludge	Weeks	264
Synthesizing Gases	Siebert	1035
Tanning Compound	McWhirter	177
Tar Paint Manufacture	Raschig	264
Therapeutic Compound	Hug	879
Thorium from Monazite	Koss	879
Tinning and Leading Metals	Plathner and Dorn	709
Tungstous Oxide, Fine	Farkas	709
Vanadium Extracted from Carnotite Concentrates	Fischer	440
Vanadium, Purifying	Blecher	878
Varnishes	Meunier	879
Zinc, etc., Production of	Pescatore	531
Zinc Recovered and Roasting Ores	Reed	879
Zinc Sulfid	Koetschet and Meyer	709

RADIUM and Uranium Situation (Editorial)	C. L. Parsons	356
Radium Market	Note	780
Radium Resources, American	C. L. Parsons	943
Rare Earth Minerals: Geol. Surv. Note on Texas Deposit		350
Recent Inventions	C. L. Parker	88, 176, 264, 353, 440, 531, 623, 709, 789, 878, 963, 1034
Recent Journal Articles, Classified List	D. D. Berolzheimer	87, 175, 263, 352, 439, 529, 622, 708, 788, 877, 962, 1034
Refractometer, Immersion, Used in Examining American Beers from Malt and Unmalted Cereals	R. Schwarz	660
Research, Editorial		966
Research Bureau of Chemists' Club	Editorial	268
Research Fund of Am. Electrochem. Soc.	W. R. Whitney	432
Research, Industrial, in America. Presidential Address at 48th Meeting	A. C. S., Rochester. A. D. Little	793
Resinous and Bituminous Substances, Classification	H. Abraham	11
Resinous Woods, Waste, Pulp and Other Products from	Note	427
Resins, Oleo-, of Jeffrey and Singleleaf Pines	A. W. Schorger	971
Rosin in Paper, Quantitative Determination of	C. F. Sammet	732
Note on	M. L. Griffin	960
Rotameter Indicator for Volumes of Gases or Liquids Consumed	Note	865
Rubber Analysis, Electric Desiccator	L. J. D. Healy	489
Rubber Chemistry Section A. C. S. D. Whipple, Secretary		
48th Meeting (Rochester) Report		956
Rubber Consumption and Production in 1912	Note	254
Rubber Extractions by Adapted Wiley Extractor	C. P. Fox	417
Rubber Goods, Sampling of	J. B. Tuttle	618
Rubber Industry, Some Problems of	Note	775
Rubber in Hawaii	Note	515
Rubber, New Method for Direct Determination	L. G. Wesson	398
Rubber, Wild Lettuce	C. P. Fox	477

SACCHARIN in Foods, Determination of	H. Durand	987
"Sacchulose", Wood Sugar	Note	166
Salines of the U. S., Composition of	III. Brines from Oceans and Salt Lakes. J. W. Turrentine	987
Salines in Silver Peak Marsh, Nevada, Analyses	R. B. Dole	19
Salt Industry of Russia	Note	196
Salt, Manufacture of, by Hodgkinson Process	Note	1024
Samples, Analyzed, Bureau of Standards. Announcement		698
Sampling Ice Cream	J. O. Halverson	528
Sampling of Coal. Preliminary Report of Am. Soc. T. M. and A. C. S. Committee	A. C. Fieldner	409
Saratoga Mineral Waters. Recent Analyses	L. R. Milford	518
Schneiwind, Dr. F. W. C. Obituary	T. J. Parker	II, 24; III, 557
Scientific Societies	—, —, —, 342, 429, 517, 611, 701, 781, 868, 956, 1030	
Separator for Dry Material	Note	864
Serpik Process for Aluminum Nitride Manufacture	J. W. Richards	335
Sewage and Sewage Effluents, Standards for	Note	427
Sewage Decomposition, Anaerobic, Gases Formed in	R. H. Jesse, Jr.	636
Sewage Disposal in New York	Note	1028

Sewage Disposal with Recovery of Plant Food Elements	W. McMurtrie	156
Sewage, Slate-Red Treatment of	Note	163
Sewage Sludge, Destructive Distillation of	A. H. Fiske and R. B. Earle	186
Sewage Sludge, Gas Manufactured from	Note	700
Sewage Treatment Methods, European	Note	1025
Sewage, Utilization of	G. A. Soper	860
Sewer Pipe Failures, Causes and Prevention of	Note	863
Shellac, American Alcohol Insoluble Test for	Committee Report U. S. Shellac Importers' Association. C. T. Bragg, Chairman	435
Shicon, Cast, Uses of	Note	257
Silicon Carbide, "Silic"	Note	775
Silk, Artificial, Industry, Progress of	Consular Note	873
Silk, Defective Artificial, Trade Note		260
Silver Determination by Gay-Lussac Method	F. P. Dewey	209
Silver Peak Marsh, Nev., Composition of Salines	R. B. Dole	196
Slag, Granulation of	Note	780
Smoke Nuisance	R. C. Benner and J. J. O'Connor, Jr.	587
Soap, Determination of Sodium Borate	P. Poetschke	645
Soaps, Cold-Process, Manufacture in Egypt	Note	774
Soda Liquors, Waste, Utilization of	Note	79
Soda Markets, Caustic and Ash	Note	251
Soda Water Deterioration Due to Microorganisms	N. P. Sherwood and C. C. Young	577
Soil Analyses. Influence of Lime-Magnesia Ratio	P. L. Gile and C. N. Ageton	33, 564; O. Loew, 257, 959
Soil Analysis, Mineralogical	W. J. McCaughey	562
Soil Nitrification, Influence of Preceding Crop	T. L. Lyon and J. A. Bizzell	136
Soil Phosphates, Effect of Ignition on Solubility of	G. S. Fraps	416
Soil Phosphoric Acid, Insoluble in Hydrochloric Acid, Condition of	W. H. Fry	664
Soil Water Question in British Guiana, An Interesting	M. Bird	1012
Soils, Citrus, Fertilization of	A. Smith and H. E. Billings	415
Soils: Composition of Sediments from Potomac and Shenandoah Rivers	J. G. Smith and W. H. Fry	1009
Soils, Estimation of Lime Requirement of	J. A. Bizzell and T. L. Lyon	1011
Soils: Methods for Carbonates	E. W. Gaither	138
Soils, Mineralogical Analysis of	W. H. Fry	30
Soot and Cinder Arrester, A German	Note	696
Spectra, Some Projection Experiments with	H. E. Howe	578
Spelter Analysis, New Technical Method of	E. J. Ericson	401
Sponges as a Fertilizer	J. G. Smith	850
Spray: Calcium Thioarsenate	S. H. Katz and P. D. Buckminster	663
Stability Test for Explosives, Modified Form	H. C. P. Weber	641
Stand, Combination, for Apparatus	E. R. Squibb and Sons	490
Starch Industry, British	Note	165
Starch in Paper, Polarimetric Method for	C. E. G. Porst and H. A. Crown	304
Statistics for Germany, 1912	Note	337
Steam Meter "Rhenania"	Note	423
Steel and Iron Corrosion	Editorial. W. H. Walker	444
Steel and Iron Corrosion, Electrolytic Prevention	J. K. Clement and L. V. Walker	361
Steel and Iron, Fusion Method for Sulfur in	F. H. Franklin	839
Steel and Iron Industry, Editorial	G. D. Chamberlain	357
Steel and Iron, Oxygen Determination	R. H. McMillen	123
Steel and Iron, Protection by Paint Films	N. A. Dubois	968
Steel and Iron, Titanium in, by Colorimetric Method	C. R. McCabe	735
Note		872
Steel Castings, Microstructure of	W. Tassin	713
Steel, Colorimetric Determination of Chromium in	F. Garratt	298
Steel, Copper Covered	J. O. Handy	884
Steel Corporation: Official Tonnage Report for 1912	Note	424
Steel Corrosion Affected by Copper	D. M. Buck	447
Steel, Determination of Chromium and Vanadium in a Correction	D. J. Demorest	84
Steel, Determination of Oxygen in	C. M. Johnson	295
Steel Exposed to Air and Fresh Water Alternately, Tests of Paints for	P. H. Walker and S. S. Voorhees	899
Steel, Finished, Production in 1912	Note	867
Steel Furnace, the Electric, Recent Developments in	P. L. V. Heroult	47
Steel Hardened with Compressed Air	Note	695
Steel Industry, Electric, Progress of	Note	866
Steel Ingots, Sound, Further Investigations for Securing	Note	424
Steel, Vanadium and Ferrovandium, Phosphorus in	C. F. Sidener and P. M. Skartvedt	838
Steel, Vanadium in, by the Hydrogen Peroxide Color Method	C. R. McCabe	736
Steel, Vanadium, Production of, in 1912	Note	695
Steels Containing Vanadium, Determination of Phosphorus in	J. R. Cain and F. H. Tucker	647

Still, Laboratory Column. H. K. Benson.....	1018	VALVE, Eynon Evans Flanged Blow-off. Note.....	605
Stones, Precious, Synthesis of. I. H. Levin.....	495	Valve for Desiccators. N. Smith.....	235
Sugar Beet: Relation between its Weight and the Composition of Its Juice. J. A. Harris and R. A. Gortner.....	192	Vanadium and Chromium in Steel, Determination of. Correction. D. J. Demorest.....	84
Sugar Factory Waste Waters Purified by "Humin." Note.....	515	Vanadium in Steel by the Hydrogen Peroxide Color Method. C. R. McCabe.....	736
Sugar from Wood. "Sacchulose." Note.....	166	Vanadium Steel and Ferro-Vanadium, Method for Phosphorus in. C. F. Sidener and P. M. Skartvedt.....	838
Sugar, Industrial Uses of. Note.....	608	Vanillin Solution, Standard, for use with Folin's Method. O. E. Harder.....	619
Sugar Industry in the U. S. Present Status. Note.....	254	Varnishes and Paints, Practical Accelerated Test. A. M. Muckenfuss.....	535
Sugar Manufacture, Technical and Chemical Control of. D. L. Davoll, Jr.....	231	Vinegar, Detecting Adulteration of Cider, with Distilled. S. L. Crawford.....	845
Sugar Polarizations, Use of Light Filter Cell. A. H. Bryan.....	167	Vinegars, Cider, Made by Generator Process, Composition of. L. M. Tolman and E. H. Goodnow.....	928
Sulfate in Ammonium Sulfate Solution, Gas Testing. R. S. McBride and E. R. Weaver.....	469	Viscosimeter, Accurate and Practical. A. Note. R. H. Twining.....	349
Correction.....	619	Viscosimeter, N. Y. Testing Laboratory, for Melting Points of Greases. H. W. Mahr.....	674
Sulfide Ores: New Desulfurizing Method. Note.....	595	Viscosimeter, Why Not a Standard? Note. W. F. Paragher.....	167
Sulfite Cooks, Testing Liquid in. Note.....	951	Volatile Matter in Coal. Preliminary Report of Am. Soc. T. M. and A. C. S. Committee. S. W. Parr.....	522
Sulfite Liquor, Spent, Tannic Acid from. Note.....	955	WALDEN, Dr. Paul. Biography and Bibliography. G. F. Kunz.....	611
Sulfite Liquor, Waste. Notes.....	78, 166, 1024	Waste Liquors Saved by Arletter Apparatus. Note.....	256
Sulfite Liquor, Waste, as a Fertilizer. Note.....	513	Water: Colorimetric Estimation of Free Chlorine in Small Amounts by Ortho-Tolidine. J. W. Ellms and S. J. Hauser.....	915
Sulfur Determinations, Simple Gasoline Gas Generator. C. E. Waters.....	853	Correction.....	1030
Sulfur Dioxide in Gelatin. P. Poetschke.....	980	Water Disinfections by Hypochlorite, Baltimore. J. B. Thomas and E. A. Sandman.....	476
Sulfur Dioxide Removed from Smelter Fume by Thiogen Process. Note.....	338	Water Filtration, Abuses in. Note.....	255
Sulfur in Coal. Preliminary Report of Am. Soc. T. M. and A. C. S. Committee. Perry Barker.....	524	Water of Crater Lake, Ore., Analysis. W. Van Winkle and N. M. Finkbinder.....	198
Sulfur, Influence of, on Stability of Iron Carbide in the Presence of Silicon. Note.....	605	Waterproofing Concrete Structures. Conclusions of Am. Soc. Testing Materials Committee. Note.....	1027
Sulfur in Illuminating Gas. R. S. McBride and E. R. Weaver.....	474	Water Purification by "Allophanoids." Note.....	79
Sulfur in Illuminating Gas. Note.....	162	Water Purification by Lime. Note.....	75
Sulfur in Iron and Steel, Fusion Method for. F. H. Franklin.....	839	Water Purification in the Industries. Note.....	163
Sulfur in Pyrites Cinder, Rapid Determination. A. B. Conner.....	399	Water Meter, The Hammond. Note.....	428
Sulfur Mining in Texas. Note.....	337	Water, Soil, Question in British Guiana, An Interesting. M. Bird.....	1012
Sulfuric Acid Chamber, New High Form. F. J. Falding and W. R. Cathcart.....	223	Water Sterilization at Trenton. H. C. Hottel.....	319
Suspended Matter, Theory of Removal of, from Gases. W. W. Strong.....	858	Water Supplies, Public Standards for Hygienic Purity. Note.....	426
"Syrolit," Artificial Leather from. Note.....	514	Water Supply for the Manufacturer. W. M. Booth.....	604
TANNIC Acid from Spent Sulfite Liquor. Note.....	955	Water, Winkler's Method for Oxygen in Effect of Nitrite and Its Prevention. F. E. Hale and T. W. Melia.....	976
Tannin, a Synthetic, "Neradol D." Note.....	863	Waters of Breitenbush Hot Springs, Ore., Analyses. W. Van Winkle.....	300
Tannin, Synthetic. Consular Note.....	705	Correction.....	436
Tantalum as a Substitute for Platinum. Note.....	162	Waters, Phosphates in Surface. G. S. Jamieson.....	301
Tar as a Fuel for Open-Hearth Furnaces. Note.....	252	Waters, Turbid, Examples of Efficiency of Calcium Hypochlorite in Treating. E. Bartow.....	18
Tar Distillation. P. P. Sharples.....	466	White Lead, Manufacture and Properties of Sublimed. J. A. Schaeffer.....	144
Tar Distillation in the U. S. R. P. Perry.....	151	White Lead, Toxicity of. Note.....	161
Tar Roads: Effects on Vegetation and Animals. Note.....	428	WILLARD GIBBS MEDAL AWARD.....	503
Tar, Water Gas, as a Wood Preservative. Note.....	427	Address of Acceptance. The Chemical Constitution of Resinous Phenolic Condensation Products. L. H. Baekeland.....	506
Tars, Dimethyl Sulfate Test for Small Amounts of Petroleum or Asphalt Products in. C. S. Reeve and R. H. Lewis.....	293	Correction.....	620
Tars, Oils and Pitches, Methods for Testing. S. R. Church.....	195	Chairman's Address. J. Stieglitz.....	504
Temperature Regulator, Water. Note.....	76	Presentation Address. W. D. Richardson.....	505
Testimony, Expert. Address, J. T. Ronald.....	582	William McMurtrie. Biography and Bibliography of Scientific Writings. Obituary. H. W. Wiley.....	616
Thermometers in Industrial Plants. Note.....	1024	Wood Alcohol. Abstract of N. Y. State Factory Investigating Commission's Report by C. Baskerville.....	768
Thiogen Process, Present Status of. Note.....	338	Wood Alcohol. Editorial.....	712
Thorium Consumption, United States. Note.....	781	Wood Distillation, Efficiency Studies. Editorial. L. F. Hawley.....	445
Thymol, Creosols and Phenol, Rapid Volumetric Method for. L. V. Redman, A. J. Weith and F. P. Brock.....	831	Wood Distillation Plant. H. K. Benson and M. Darrin.....	935
Tin in Canned Foods, an Electrolytic Method. A. S. Cushman and E. B. Wettengel.....	217	Wood Preservation. Note.....	163, 252
Tinning Industry. Note.....	423	Wood Preservative, Water Gas Tar. Note.....	427
Titanium in Iron and Steel by Colorimetric Method. C. R. McCabe.....	735	Wood Preservatives, Commercial Value Tests. H. F. Weiss.....	372
Note.....	872	Wood Preserving Oils, Antiseptic Tests. A. L. Dean and C. R. Downs.....	126
Towers, Absorption and Reaction, for Chemical Works. Note.....	865	Wood Pulp, Consumption in Canada. Note.....	774
Tubing, Gilled. Note.....	161	Wood Sugar, "Sacchulose." Note.....	166
Tubing, Theta. Note.....	76	Wood Waste, Utilizing. J. E. Teeple.....	680
Tungsten, Ductile, Applications of. C. G. Fink.....	8	YEAST and Bacteria, Influence of Ozone on. C. A. Nowak.....	668
Tungsten Filament Lamps. Note.....	697	ZINC Determined in Treated Ties. F. C. Frary and M. G. Mastin.....	738
Tungsten Powder, Determination of Oxygen in. C. M. Johnson.....	295	Zinc Extracted by Bisulfite Process. Note.....	513
Turpentine Industry, French. Note.....	77	Zinc in Ores, Determination of. D. J. Demorest.....	302
UNIVERSITIES and Chemical Industries. M. T. Bogert.....	757		
Uranium and Radium Situation. Editorial. C. L. Parsons.....	356		
Urea and Nitrous Acid. Rate of Reaction in Dilute Solutions. W. D. Bonner and E. S. Bishop.....	134		





TP
1
Il3
v.5

I&EC. Industrial and
engineering chemistry

Engin.

ENGINE STORAGE

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY
